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RESEARCH PAPER RP784

Part of Journal of Research of the National Bureau of Standards, Volume 14, May 1935

THERMAL EXPANSION OF MONOCRYSTALLINE AND POLYCRYSTALLINE ANTIMONY

By Peter Hidnert

ABSTRACT

Measurements were made on the linear thermal expansion of eleven samples of single crystals of antimony and three samples of polycrystalline antimony at various temperatures between 20 and 560° C, and the data were correlated with the results obtained by previous investigators to 300° C. The linear expansion depends upon the direction along which the measurements are made. For example, the linear expansion along the trigonal axis (0° orientation) of a single crystal is about twice as large as the expansion along a direction perpendicular to this axis (90° orientation). Equations were derived which show the relationships between the coefficients of expansion and the orientations of single crystals.

The linear thermal-expansion curves of polycrystalline antimony show that there is no polymorphic transition between 20 and 560° C. The differences in the linear expansion of different samples of polycrystalline antimony are attributed to variations in the average orientation of the crystals. Figure 13 shows a comparison of the linear thermal expansion of monocrystalline and polycrystalline antimony.

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I. INTRODUCTION

It has been pointed out by Carpenter[1] that the scientific investigation of metals in the future will have to take into account both the monocrystalline and the polycrystalline states, and the variations in any particular property which may be secured by varying the orientation of the crystal. The properties of a specimen of polycrystalline metal depend upon the extent of crystallization, the nature of the crystals, their magnitude and their orientation, as well as upon the admixture of foreign crystals and the presence of impurities. Such knowledge should form the basis of the scientific manufacture of metals and alloys possessing specified properties. Promising applications have already appeared in the field of metallurgy.

[1] Carpenter, Nature, **126**, 17 (1930).

Antimony[2] crystallizes in the rhombohedral form of the hexagonal system. It is one of the metals that is anisotropic and therefore some of its properties, such as thermal expansion, depend on the orientation of the crystals. Data on the thermal expansion of single crystals of antimony are fundamental, for they are necessary in order to understand the behavior of this metal in the polycrystalline state.

Fizeau in 1869, and Bridgman in 1925, reported data on the linear thermal expansion of monocrystalline antimony for temperature ranges between 0 and 100° C. Between 1754 and 1910 a number of investigations were made on the thermal expansion of polycrystalline antimony for various temperature ranges between −190 and +100° C. In 1920 Braesco reported coefficients of linear expansion of polycrystalline antimony between 100 and 300° C. No data have been found in the literature for higher temperatures.[3] Tables 1 and 2 give summaries of available data by previous observers on the thermal expansion of monocrystalline and polycrystalline antimony.

TABLE 1.—*Summary of expansion data by previous observers on monocrystalline antimony*

Observer	Date	Reference	Material	Temperature or temperature range	Coefficient of linear expansion per degree centigrade
				°C	×10⁻⁶
Fizeau	1869	Compt.rend. **68**, 1125 (1869), or Ann. Phys. **138**, 26 (1869).	Antimony crystal:		
			Parallel to axis	40	16.9
				0 to 100	16.8
			Perpendicular to axis	40	8.8
				0 to 100	9.0
Bridgman	1925	Proc. Am. Acad. Arts Sci. **60**, 305 (1924–25). See also Proc. Acad. Sci. **10**, 411 (1924).	Antimony, in single grain casting:		
			Parallel to axis [1]	15 to 25	13.6
			Perpendicular to axis [1]	15 to 25	8.0

[1] Specimen cut from a large casting.

The present investigation was undertaken in order to extend our knowledge of the linear thermal expansion of monocrystalline and polycrystalline antimony above these temperatures, and to determine the effect of orientation on thermal expansion. Eleven samples of single crystals of antimony and three samples of polycrystalline antimony were investigated at various temperatures between 20 and 560° C.

[2] The principal uses of antimony have been given by Chung Yu Wang in a book entitled Antimony (C. Griffin & Co., London, 1909).

[3] Roeser, Schofield, and Moser, Melting point of antimony, 630.5° C. BS J. Research **11**, 1 (1933) RP573.

TABLE 2.—*Summary of expansion data by previous observers on polycrystalline antimony*

Observer	Date	Reference	Material	Temperature or temperature range	Coefficient of linear expansion per degree centigrade	Remarks
				°C	$\times 10^{-6}$	
Smeaton	1754	Phil.Trans. **48**, part 2, 598 (1754)	Antimony	0 to 100	10.8	Computed from Smeaton's data.
Kopp	1852	Ann.Chem.Pharm. **81**, 1 (1852)	do	12 to 42		Average coefficient of cubical expansion 33×10^{-6} per degree C, obtained by density method.
Calvert, Johnson and Lowe.	1859	Rept.Brit.Assoc. **28**, 46 (1859); Proc. Roy.Soc. (London) **10**, 315 (1859–60); Chem.News **3**, 315, 357, 371 (1861).	Antimony, cast	0 to 100	9.8	
Matthiessen	1866	Phil.Trans. **156**, 861 (1866) or Ann. Phys. **130**, 50 (1867).	Antimony, gilded [1]	0 to 100		Average coefficient of cubical expansion 31.7×10^{-6} per degree C, obtained by weighing two samples in water at different temperatures.
Le Chatelier	1899	Compt.rend. **128**, 1444 (1899)	Antimony	63	10.	
Dorsey	1907	Phys.Rev. **25**, 88 (1907)	Antimony, cast (density = 6.88).	−170	7.5	These coefficients were obtained by Dorsey from his data on cooling and warming the specimen several times. The specimen expanded more on warming than it contracted in cooling.
				−150	7.9	
				−130	8.4	
				−110	8.9	
				−90	9.1	
				−70	9.3	
				−50	9.6	
				−30	9.7	
				−10	9.9	
				+10	10.1	
				−180 to +20	8.2	
Lussana	1910	Nuovo cimento [5] **19**, 182 (1910)	Antimony [2] (from Merck) fused in cylinder.	9 to 58		Between 9 and 58° C, obtained following average coefficients of cubical expansion: 34.4×10^{-6}, 32.7×10^{-6} and 31.7×10^{-6} at 1, 1,000, and 1,500 atmospheres, pressure, respectively. Similarly for the range between 9 and 72° C. obtained the following average coefficients of cubical expansion: 35.3×10^{-6}, 32.9×10^{-6}, and 31.7×10^{-6}.
				9 to 72		
Grüneisen	1910	Ann.Phys. [4] **33**, 33, 65 (1910)	Antimony (from C. A. F. Kahlbaum).	−190 to +17	10.2	
				+17 to 100	10.9	
				18	10.7	
Braesco	1920	Compt. rend. **170**, 103 (1920) and Ann. Phys. **14**, 6 (1920).	Antimony, agglomerated [3] and quenched.	100 to 300	8.3	In the second publication, Braesco states the coefficients of expansion apply at 100° C.
			Antimony, agglomerated [3] and annealed.	100 to 300	8.3	
			Antimony, cast and quenched.	100 to 300	10.0	
			Antimony, cast and annealed.	100 to 300	10.0	
Jubitz	1926	Z.tech.Phys. **7**, 522 (1926)	Antimony, cast	20 to 40	10.1	Computed from data of observer.
			Antimony, drawn	20 to 40	8.8	

[1] The samples were gilded to prevent action of water.
[2] Specific gravity 6.6848 at 9.1° C referred to water at 4° C as unity.
[3] Powdered antimony cemented with a small amount of silicate of soda.

II. MONOCRYSTALLINE ANTIMONY

1. MATERIALS INVESTIGATED

Eleven samples of single crystals of antimony prepared by Prof. P. W. Bridgman of Harvard University, were used in this investigation. These were prepared by slow solidification from the melt. This method[4] of growing single crystals was described[5] by him about ten years ago.

These samples cover a range of orientation[6] from 32° to 90°. Most of the orientations are between 60° and 90°, for the preferred manner of growth is with the trigonal[7] axis perpendicular to the axis of the rod (90° orientation). The author made a number of attempts to obtain a few antimony crystals having orientations between 0° and 32°, but he was unsuccessful in obtaining any of these crystals from various laboratories in this country or the National Physical Laboratory in England. Mildred Allen[8] also experienced difficulty in obtaining single antimony crystals having small orientations for an investigation on the effect of tension on the electrical resistance. She obtained only two readings for orientations less than 50° and stated "This came about for two reasons: it is comparatively difficult to grow crystals with the principal cleavage plane nearly perpendicular to the cylindrical length, and, more important, crystals with such orientations are so exceedingly brittle that it is very nearly impossible to mount them in the apparatus without sufficient jarring to break them along a principal cleavage."

Goetz and Hasler[9] observed that the probable orientation of bismuth single crystals, which are similar to antimony crystals, was between 30° and 90°, the orientation of 0° never occurring at all. They state that one influence can be considered as resident in the strain applied to the crystal during the act of crystallization by the glass walls, and due to the expansion of the metal at the melting point. "Hence, the volume of crystallizing region reaches a maximum and then decreases due to the thermal contraction during the cooling process. From the observations by the authors, it is probable that the orientation of the crystal becomes rigidly determined at the instant when a decided contraction appears, preceded by the above expansion indicating that the properties of the crystal (orientation, perfection, etc.) are determined by the forces acting at the time of this contraction to a large extent. This may be observed in certain cases by watching an upright glass tube, filled with molten bismuth, as the crystal grows upward from a cooled tip. The crystallization is seen to take place in blocks which contract visibly from the glass at the instant of formation. If one considers that the stresses, induced by previous expansion, are present at the moment of contraction, then the difficulty of obtaining crystals with small orientations may be

[4] There are four methods of growing single crystals, (1) from the vapor, (2) from the melt, (3) from solution, and (4) from the solid.

[5] Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1924–25).

[6] The term orientation is defined as the angle between the trigonal axis of the single crystal and the geometric axis of the rod along which the expansion was measured.

[7] The lattice structure (determined by James and Tunstall, Phil. Mag. **40**, 233 (1920) and Ogg, Phil. Mag. **42**, 163, (1921)) of antimony is a lattice of trigonal symmetry composed of two similar face-centered rhombohedral lattices, similarly oriented, displaced relative to each other along the longest diagonal of the rhombohedron (the axis of trigonal symmetry). The unit rhomb contains 8 atoms and the length of the edge of the unit rhomb is 6.20×10^{-8} cm.

[8] Mildred Allen, Phys. Rev. **43**, 569 (1933).

[9] Goetz and Hasler, Proc. Nat. Acad. Sci. **15**, 646 (1929).

explained as follows. As it is known that the coefficient of thermal expansion is largest parallel to the trigonal axis and smallest normal to it, it could be expected that the crystal prefers an orientation in the glass tube where the maximum contraction would be parallel to the direction of maximum compression. Thus large angle-orientations are preferred."

The direction of the trigonal axis of each antimony single crystal was most conveniently obtained from the principal cleavage plane, which is perpendicular to the axis. The principal cleavage plane may be distinguished from the secondary cleavage planes, because the cleavage on the principal plane is easier, more extensive, and noticeably more nearly perfect than on the secondary planes.

The angle between the principal cleavage plane and the axis of each rod was measured,[10] and from this measurement the orientation, or the angle between the trigonal axis of the crystal and the axis of the rod, was computed. The cleavage planes and the orientations were checked by Dr. S. B. Hendricks of the Bureau of Chemistry and Soils of the U. S. Department of Agriculture. The identification of the cleavage planes of samples 1524, 1527, and 1529 (see table 3) was ascertained by him by reflection of Cu Kα radiation from the perfect cleavage. "The angle of reflection was 11°52′, corresponding to the required angle for (111), referred to rhombohedral axes." He measured the spacing of the imperfect cleavage plane for sample 1532 and found it to correspond to that required for (110). Dr. Hendricks identified the cleavage planes of the other samples by inspection.

TABLE 3.—*Length and orientation of single crystals of antimony*

Sample	Length	Orientation	Sample	Length	Orientation
	Millimeters	*Degrees*		*Millimeters*	*Degrees*
1524	52.1	72	1530	59.0	77
1525	54.8	69	1531	67.6	74
1526	69.0	63	1532	33.7	90
1527	40.5	73	1553	20.6	90
1528	36.7	32	1553A	20.9	90
1529	32.8	32			

Table 3 indicates the length and the orientation of each single crystal. All samples except 1553 and 1553A have a circular cross section with the diameter about 3.5 mm. Samples 1553 and 1553A were cut from a piece[11] of a large single crystal (about 22-mm diameter) made a number of years before the other samples were prepared. The cross sections of samples 1553 and 1553A are nearly square, with the edge of the square about 3 mm.

The single crystals of antimony were made from "Kahlbaum grade" antimony purchased by Prof. Bridgman from Akatos, Inc., in New York City. Samples 1524 to 1532, inclusive, were made from antimony obtained in 1932, and samples 1553 and 1553A were prepared from antimony purchased about 1923. No chemical analyses were made.

As the single crystals are very fragile, Prof. Bridgman sent them to the National Bureau of Standards in a tube filled with venice

[10] By D. R. Miller of this Bureau.

[11] It was not possible to cut a sample with an orientation of 0° from this piece, for the layers of metal separated on cutting.

turpentine. The entire tube in which they were contained was heated on a water bath until the venice turpentine was sufficiently fluid to allow the removal of the crystals. Before expansion determinations were started on each sample, it was soaked in acetone several days, washed with a soap solution, then water, and finally alcohol, in order to remove any deposit of venice turpentine.

2. APPARATUS

The fused-quartz-tube expansion apparatus described by Hidnert and Sweeney [12] was modified so that the short single crystals of different lengths (21 to 69 mm) could be used without cutting the fragile samples to the same length. A 45-cm movable fused-quartz rod was used for all samples except 1526 and 1531. For these two samples, a 41-cm movable fused-quartz rod was employed. These movable rods are hollow, but are closed at the ends. The bottom of each movable rod is concave and the top is flat.

Two collars (made from a heat-resisting alloy and a ceramic material) and a porcelain tube supported the sample centrally in a vertical fused-quartz tube closed at the lower end, which was ground concave. A movable fused-quartz rod (41 or 45 cm) rested on top of the sample and extended above the open end of the tube. An indicator gage graduated to 0.0001 inch, rested on top of the movable fused-quartz rod. A chromel-alumel thermocouple placed inside the fused-quartz tube near the center of the sample indicated the temperature. An electric furnace surrounding the tube containing the sample was used for heating.

The indicator gage fastened near the top of the tube registered the differential expansion between the sample and an equivalent length of fused quartz. A correction for the small expansion [13] of fused quartz was made.

Figures 1 and 2 of BS Research Paper RP29 show photographs of the fused-quartz-tube apparatus and auxiliary equipment. Blueprints of the apparatus are available for persons interested in constructing this equipment.

3. RESULTS

Measurements were made on the linear thermal expansion of the single crystals of antimony at various temperatures between 20° and 500° C. Two or three tests were made on each sample. The results obtained on heating and cooling are shown in figures 1 and 2. The expansion curves are plotted from different origins in order to show the individual characteristics of each curve.

The results obtained in the first heating and cooling indicate that the single crystals of antimony behave like cast metals or alloys as far as strains are concerned, for the observations on cooling do not coincide with the expansion curves on heating. This is in agreement with Davey's statement [14] that all crystals are produced in a state

[12] Hidnert and Sweeney, BS J. Research **1**, 771 (1928) RP29.
[13] Souder and Hidnert, BS Sci. Pap. **21**, 1 (1926–27) S524.
[14] Davey, Phys. Rev. **29**, 206 (1927).

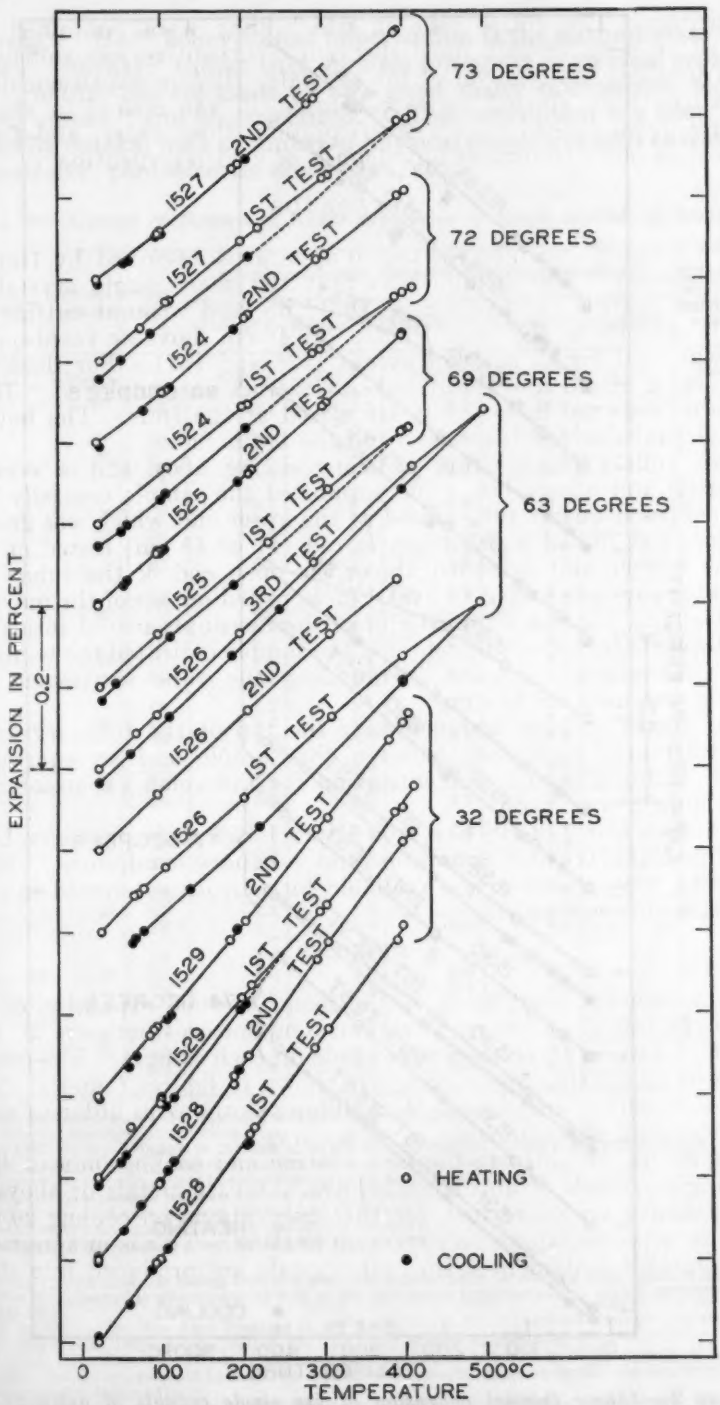

FIGURE 1.—*Linear thermal expansion of six single crystals of antimony with orientations from 32 to 73 degrees.*

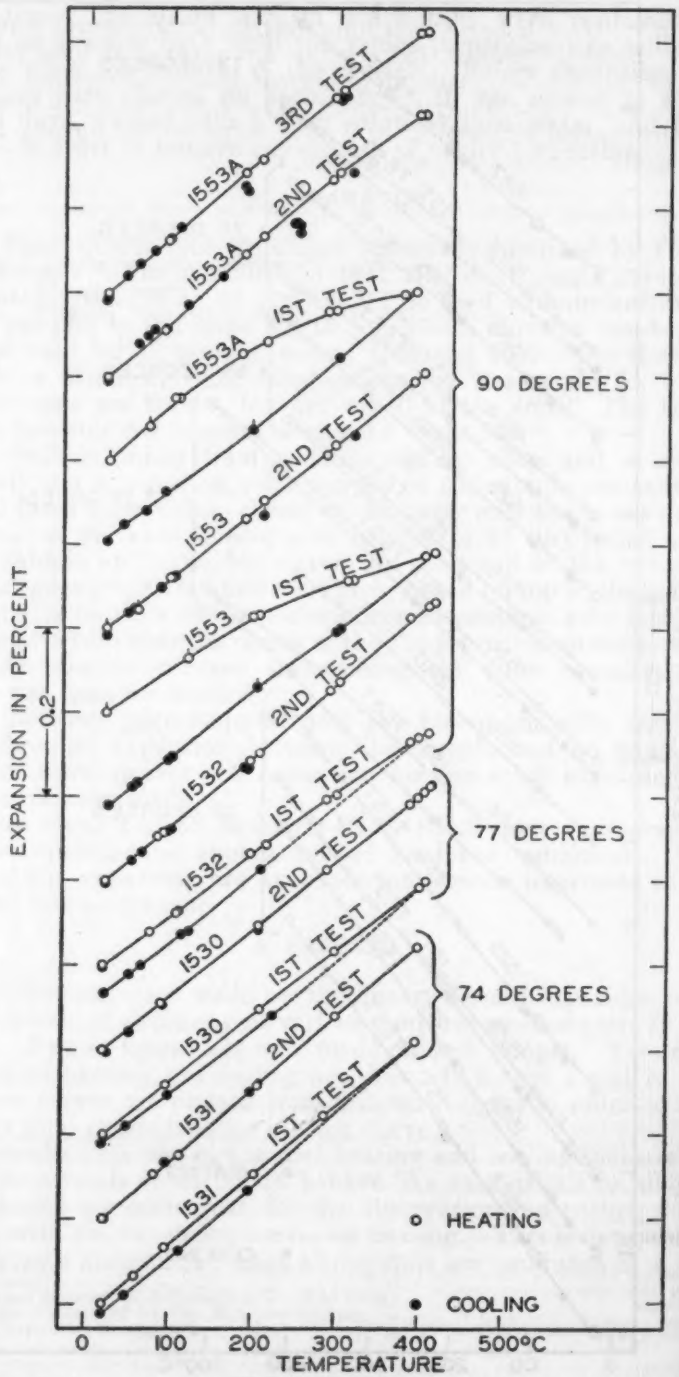

FIGURE 2.—*Linear thermal expansion of five single crystals of antimony with orientations of 74, 77, and 90 degrees.*

[A tagged symbol indicates more than one observation]

of strain.[15] He [16] believes that imperfection is the natural state of a crystal. Smekal [17] thinks that crystals are never of an ideal geometrical structure but are made up of a great many microscopic blocks leaving cracks [18] and imperfections.[19] This conception has been correlated by Smekal with a number of physical properties such as electric conductivity, photoelectric absorption, etc.

TABLE 4.—*Average coefficients of linear expansion of single crystals of antimony*

Sample	Orientation [1]	Test no.[2]	Average coefficients of expansion per degree centigrade					Change in length after heating and cooling [3]
			20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C	20 to 500° C	
	Degrees		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
1528	32	1H [4]	13.3	13.5	13.4	13.3		+0.01
		2H [4]	12.4	13.3	13.5	13.4		.00
1529	32	1H	12.6	12.4	11.8	12.1		−.01
		1C	11.4	12.2		12.3		
		2H [4]	11.4	11.6	12.0	12.1		−.00
1526	63	1H	10.1	9.4	9.3	9.1	8.6	−.05
		1C	9.1	9.0		9.5	9.6	
		2H	9.6	9.4	9.3	9.0		
		3H	9.5	9.5	9.5	9.6	9.2	−.02
		3C	9.4	9.5	9.6	9.6	9.6	
1525	69	1H	9.1	8.5	8.6	8.4		−.02
		1C	9.0	8.5		8.8		
		2H [4]	9.0	8.7	8.8	8.8		+.00
1524	72	1H	8.1	8.0	7.8	7.5		−.03
		1C	7.4	7.9		8.2		
		2H [4]	7.7	8.3	8.2	8.1		−.01
1527	73	1H	8.7	8.4	8.1	7.9		−.02
		1C	8.8	8.1		8.5		
		2H [4]	7.5	8.1	8.3	8.2		−.01
1531	74	1H	8.7	8.4	8.4	8.3		−.01
		1C	8.0	8.3		8.6		
		2H [5]	8.5	8.6	8.6	8.5		−.00
1530	77	1H	7.9	8.0	7.8	7.7		−.01
		1C	7.2	7.3		7.9		
		2H [5]	7.8	7.9	8.0	7.9		−.01
1532	90	1H	7.2	7.5	7.3	7.2		−.03
		1C	7.4	7.8		8.0		
		2H [5]	8.3	8.2	8.4	8.4		−.00
1553	90	1H	6.6	6.4	[6]	[7]		−.11
		1C	7.8	8.0	7.6	7.7		
		2H	7.6	7.9	7.9	8.0		−.01
1553A	90	1H	9.0	7.8	[8]	[9]		−.09
		1C	7.5	7.4	7.7	7.9		
		2H	8.2	9.0	8.7	8.3		−.00
		3H	8.6	8.7	8.6	8.2		−.01

[1] Angle between trigonal axis of crystal and geometric axis of sample.
[2] H indicates heating and C cooling.
[3] The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length
[4] Observations on cooling close to expansion curve on heating (See fig. 1).
[5] Observations on cooling close to expansion curve on heating (See fig. 2).
[6] Coefficient of expansion between 200 and 300° C, 3.9×10⁻⁶.
[7] Coefficient of expansion between 300 and 400° C, 3.2×10⁻⁶.
[8] Coefficient of expansion between 200 and 300° C, 4.6×10⁻⁶.
[9] Coefficient of expansion between 300 and 400° C, 2.2×10⁻⁶.

[15] Davey (see footnote 14) stated that this accounts satisfactorily for etching pits, dendrite formation and other metallographic phenomena as well as the customary imperfections in crystal structure noted in X-ray work.
[16] Davey, Trans. Am. Soc. Steel Treating **21**, 965 (1933).
[17] Smekal, Z. tech. Phys. **7**, 535 (1926); **8**, 561 (1927); and several other papers.
[18] Kapitza, Proc. Roy. Soc. **119**, 358 (1928), proved the existence of cracks in single crystals of bismuth. He showed that the cracks could be closed by application of external pressure, so that the electric resistance was diminished correspondingly.
[19] Imperfections of crystals may be of either mechanical or chemical nature. See Zwicky, Proc. Nat. Acad. Sci. **15**, 253 (1929).

Most of the expansion curves on heating are irregular or concave towards the temperature axis. The expansion curves of samples 1553 and 1553A in the first heating show a "flattening" between 200 and 400° C. In order to determine if this phenomenon was caused by evolution of gas from these samples, a piece of the antimony crystal (as received) from which samples 1553 and 1553A were cut, was subjected to analysis [20] by the vacuum fusion method. The results indicate that the evolution of gas up to 700° C was negligible, of the order of magnitude of the blank correction for the apparatus. The same results were also obtained on sample 1553 after the expansion tests had been completed. It therefore appears that the "flattening" of the expansion curves cannot be accounted for by an evolution of gas.

Most of the observations on cooling are below the expansion curves on heating. The deviations between the observations on cooling and the expansion curves on heating are less in the second tests than in the first tests.

Table 4 gives coefficients of expansion which were obtained from the expansion curves on heating and cooling (figs. 1 and 2). In most cases, the coefficients of expansion are higher in the second tests on heating than in the first tests on heating.

From the coefficients of expansion obtained in the second and third tests for the range between 20 and 100° C (table 4), the following empirical equation [21] was derived by the method of least squares:

$$_{20}E_{100}=(17.17-0.1951\theta+0.0010390\theta^2)10^{-6} \quad (1)$$

where $_{20}E_{100}$ represents the average coefficient of linear expansion between 20 and 100° C, and θ represents the orientation, or the angle between the trigonal axis of a single crystal and the geometric axis of the specimen. This equation [22] applies for single crystals of antimony with orientations between 32 and 90°.

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[20] By H. C. Vacher of this Bureau.

[21] Helen D. Megaw, Proc. Roy. Soc., London [A] **142**, 198 (1933), stated that the theory of homogeneous deformation (Fizeau, 1868; Fletcher, 1880; Voigt, Lehrbuch der Kristallphysik, 1910) shows that a sphere of unit radius at a given temperature in any crystal changes at a neighboring temperature into an ellipsoid, the axes of which serve, in length and direc ion, to determine the expansion of the crystal over this temperature range. "Let the expansion coefficients in the direction of the axes be ϵ_1, ϵ_2, ϵ_3. Then the semiaxes of the ellipsoid corresponding to a temperature change of 1° C are $1+\epsilon_1$, $1+\epsilon_2$, $1+\epsilon_3$, and the expansion coefficient ϵ in any other direction making angles θ_1, θ_2, θ_3 with the axes of the ellipsoid is given by the equation

$$\frac{1}{(1+\epsilon)^2}=\frac{\cos^2\theta_1}{(1+\epsilon_1)^2}+\frac{\cos^2\theta_2}{(1+\epsilon_2)^2}+\frac{\cos^2\theta_3}{(1+\epsilon_2)^2}$$

"For purposes of calculation, it is more convenient to use Voigt's 'deformation tensor.' This is a conic with its axes in the same direction as those of the ellipsoid previously described, but involving the expansion coefficients directly. It is given by the equation

$$\epsilon=\epsilon_1\cos^2\theta_1+\epsilon_2\cos^2\theta_2+\epsilon_3\cos^2\theta_3$$

It can be derived from the previous ellipsoid by neglecting the squares of the expansion coefficients." The latter equation has been given by Fizeau, Compt. rend. **62**, 1101 (1866), who also indicated an equation of the form

$$\epsilon=\epsilon_1\cos^2\theta+\epsilon_2\sin^2\theta$$

for the case where $\epsilon_2=\epsilon_3$.

[22] The equation

$$_{20}E_{100}=13.53\times10^{-6}\cos^2\theta+7.97\times10^{-6}\sin^2\theta \quad (1a)$$

was also derived and found to apply as closely as equation 1 for the range from 32 to 90°. However, the coefficient of expansion for 0° orientation computed from equation 1a does not agree as closely with the values reported by Fizeau and Bridgman, as the value obtained from equation 1 (table 6).

A comparison of the observed coefficients of expansion and the values computed from equation 1 are given in table 5. The sum of the squares of the residuals is 3.93×10^{-12} and hence the probable error of a single computed value is equal to

$$0.6745\sqrt{\frac{3.93\times10^{-12}}{14-3}} \text{ or } \pm0.4\times10^{-6}$$

TABLE 5.—*Comparison of observed and computed coefficients of expansion of single crystals*

Orientation	Average coefficients of linear expansion per degree centigrade between 20 and 100° C		Residual	Orientation	Average coefficients of linear expansion per degree centigrade between 20 and 100° C		Residual
	Observed	Computed			Observed	Computed	
Degrees	$\times10^{-6}$	$\times10^{-6}$	$\times10^{-6}$	Degrees	$\times10^{-6}$	$\times10^{-6}$	$\times10^{-6}$
32	12.4	12.0	+0.4	73	7.5	8.5	−1.0
32	11.4	12.0	−.6	74	8.5	8.4	+.1
63	9.6	9.0	+.6	77	7.8	8.3	−.5
63	9.5	9.0	+.5	90	8.3	8.0	+.3
63	9.4	9.0	+.4	90	7.6	8.0	−.4
69	9.0	8.7	+.3	90	8.2	8.0	+.2
72	7.7	8.5	−.8	90	8.6	8.0	+.6

The following equations for temperature ranges from 20 to 200°, 20 to 300° and 20 to 400° C, were also derived by the method of least squares from the coefficients of expansion obtained in the second and third tests (table 4):

$$_{20}E_{200}=(18.88-0.2440\theta+0.001411\theta^2)10^{-6} \quad (2)$$
$$_{20}E_{300}=(19.54-0.2579\theta+0.001479\theta^2)10^{-6} \quad (3)$$
$$_{20}E_{400}=(19.49-0.2548\theta+0.001430\theta^2)10^{-6} \quad (4)$$

In these equations, $_{20}E_{200}$, $_{20}E_{300}$, and $_{20}E_{400}$ represent the average coefficients of linear expansion from 20 to 200° C, 20 to 300° C and 20 to 400° C, respectively, and θ represents the orientations in degrees of the single crystals between 32° and 90°. The probable errors of $_{20}E_{200}$, $_{20}E_{300}$, and $_{20}E_{400}$ are $\pm0.4\times10^{-6}$, $\pm0.3\times10^{-6}$ and $\pm0.3\times10^{-6}$, respectively.

Figure 3 shows comparisons of the observed coefficients of expansion obtained in the second and third tests with the curves representing equations 1 to 4. The curve representing equation 1 for the range from 20 to 100° C was extrapolated to orientation 0° in order to compare this curve with the coefficients of expansion obtained by Fizeau [23] and Bridgman [24] for crystals with 0° orientation. Their values for orientation at 90°, are also indicated in figure 3.

Equations 1 to 4 and the curves in figure 3 show that the coefficients of expansion of single crystals decrease with increase in the orientation. Coefficients of expansion of single crystals of various orientations were computed from equations 1 to 4 and are shown in table 6.

[23] See table 1.
[24] See table 1.

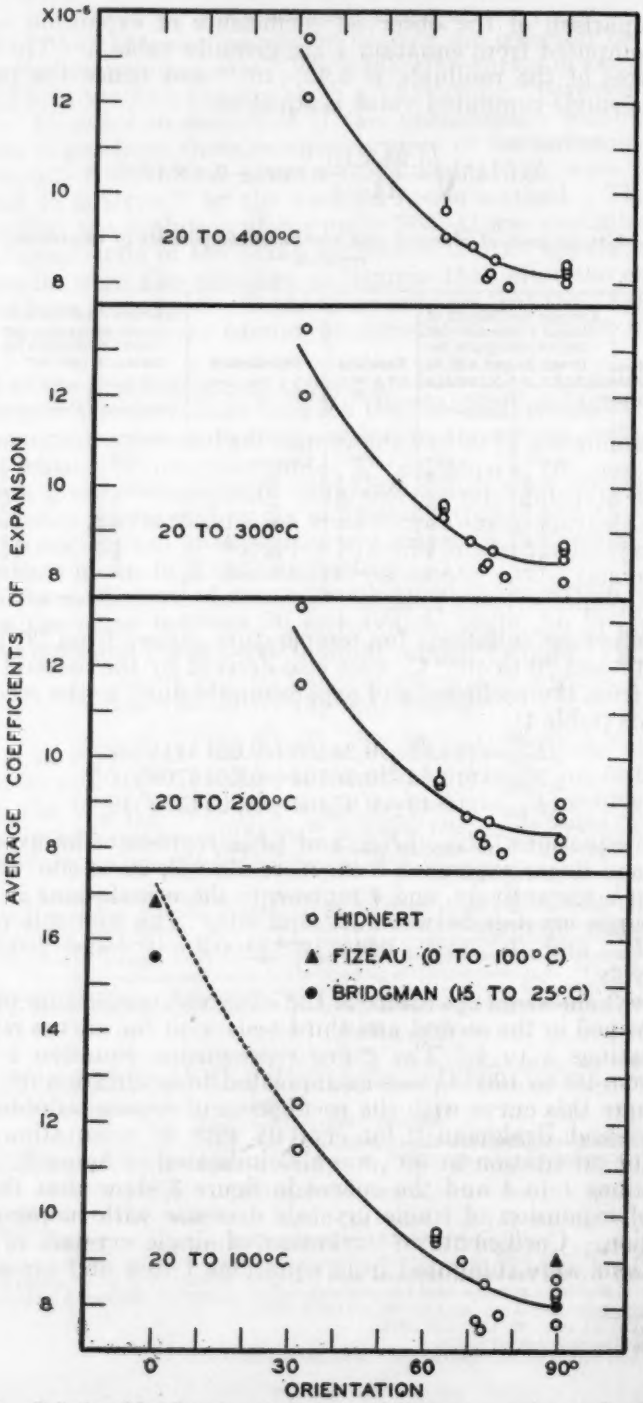

FIGURE 3.—*Relationships between coefficients of linear expansion and orientations of single crystals of antimony.*

The light circles represent observations obtained in the present investigation from which the curves (see equations 1 to 4) were derived]

TABLE 6.—*Coefficients of expansion of single crystals*

(Computed from equations 1 to 4)

Orientation	Average coefficients of linear expansion per degree centigrade			
	20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C
Degrees	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
0[1]	[2] (17.2)	(18.9)	(19.5)	(19.5)
30	12.3	12.8	13.1	13.1
60	9.2	9.3	9.4	9.4
70	8.6	8.7	8.7	8.7
80	8.2	8.4	8.4	8.3
90	[3] 8.0	8.4	8.3	8.1

[1] The coefficients of expansion in parentheses were extrapolated from equations 1 to 4.
[2] Fizeau obtained 16.8×10^{-6} between 0 and 100° C, and Bridgman 15.6×10^{-6} between 15 and 25° C.
[3] Fizeau obtained 9.0×10^{-6} between 0 and 100° C, and Bridgman 8.0×10^{-6} between 15 and 25° C.

An examination of table 6 shows that the linear expansion along the trigonal axis (0° orientation) is about twice the expansion along a direction perpendicular to this axis. Bridgman [25] has pointed out that the cleavage plane corresponds to some fundamental condition in the crystal structure which is reflected in the properties of the single crystal. The atoms are connected more loosely across the cleavage plane, so that external forces produce greater effects perpendicular to this plane (along trigonal axis) than in other directions. The results obtained on the thermal expansion of single crystals of antimony confirm the view expressed by Bridgman.

In 1866, Fizeau [26] showed that the coefficient of cubical expansion of a crystal may be represented [27] by the following equation:

$$\alpha^{cub} = \alpha + \alpha' + \alpha''$$

where α^{cub} represents the coefficient of cubical expansion, and α, α', and α'' represent the coefficients of linear expansion of the crystal along three rectangular axes. For crystals such as antimony, where the coefficients of linear expansion along two of these axes are equal, this equation becomes [28]

$$\alpha^{cub} = \alpha + 2\alpha' \qquad (5)$$

where α^{cub} represents the coefficient of cubical expansion, α represents the coefficient of linear expansion of a crystal along its axis (0° orientation) and α' the coefficient of linear expansion perpendicular to the axis (90° orientation). Coefficients of linear expanson of monocrystalline antimony along the axis (0° orientation) were computed from this equation by the substitution of 8.0×10^{-6} (table 6) for α' and of each value of the coefficient of cubical expansion [29] reported in separate investigations by Kopp, Matthiessen and Lussana (table 2). The same value for α' was assumed for the various temperature ranges between 0 and 100° C. Table 7 shows a comparison of computed and observed values for α.

[25] Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1924–1925).
[26] Fizeau, Compt. rend. **62**, 1101, 1133 (1866).
[27] By neglecting second-order terms.
[28] The present author has recently derived the following equation:

$$\alpha^{cub} = (1+\alpha)(1+\alpha')^2 - 1.$$

This equation may be reduced to equation 5 by neglecting second-order terms.
[29] The coefficient of cubical expansion is the same for monocrystalline and polycrystalline antimony.

TABLE 7.—*Comparison of coefficients of linear expansion of monocrystalline antimony along axis (0° orientation)*

Observer	Temperature range	Coefficients of expansion per degree centigrade	
		Computed [1]	Observed
	°C	$\times 10^{-6}$	$\times 10^{-6}$
Kopp	12 to 42	17	
Matthiessen	0 to 100	15.7	
Lussana	9 to 72	19.3	
Fizeau	0 to 100		16.8
Bridgman	15 to 25		15.6
Hidnert	20 to 100		[2] 17.2
Average		17.3	16.5

[1] Values for Kopp, Matthiessen, and Lussana were computed from equation 5 (Fizeau's equation).
[2] Extrapolated from equation 1 and taken from table 6.

The densities of four single crystals of antimony were determined [30] after the measurements on thermal expansion had been completed. Table 8 gives the densities obtained. All except that for sample 1553 A are in the neighborhood of the highest value obtained for the density of polycrystalline antimony (section III–1).

TABLE 8.—*Densities of single crystals of antimony*

Sample	Density [a] at 25° C
	g/cm³
1528	6.684
1525	6.687
1532	6.670
1553A	[b] 6.572

[a] Values are believed to be correct to within ±0.005.
[b] The density was redetermined by W. S. Clabaugh of this Bureau, who obtained the value 6.569.

Davey [31] has pointed out that the densities of different crystals of the same metal rarely agree exactly, for crystals do not exactly duplicate each other on account of the effect of traces of impurities on the interplanar distances and the fragmentation of the crystal.

III. POLYCRYSTALLINE ANTIMONY

1. MATERIALS INVESTIGATED

Three samples of cast polycrystalline antimony were used in the investigation. Table 9 gives information about the preparation [32] of the samples:

[30] By S. Alpher of this Bureau.
[31] Davey, A Study of crystal structure and its applications (McGraw-Hill Book Co., Inc., New York, 1934).
[32] C. M. Saeger of this Bureau prepared these samples.

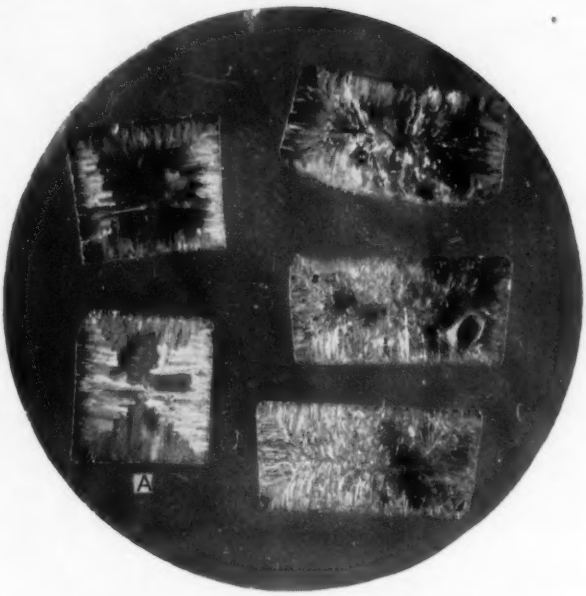

FIGURE 4.—*Two cross sections of sample 1067 (left) and three cross sections of sample 1450 (right).*

Electrolytic etch in 5 percent oxalic acid. ×2.

FIGURE 5.—*Four cross sections of sample 1450.*

Electrolytic etch in 5 percent oxalic acid. ×2.

FIGURE 6.—*Area at* A, *figure 4, showing columnar structure of sample 1067.*

Edge of sample at top, center of sample near bottom of figure. Electrolytic etch in 5 percent oxalic acid. ×30.

TABLE 9.—*Preparation, chemical composition and density of polycrystalline antimony*

Sample	Cross-section of sample [a]	Origin and preparation	Purity [b]	Density [c] at 25° C
	mm			g/cm³
1067	10×9	Antimony, Cookson's best grade (purchased from Nathan Trotter & Co., Philadelphia, Pa.), cast in a sand mold.	[d] 99.8	[e] 6.630
1450	15×7	Two bars of cast antimony, each about 15 cm long (purchased from C. A. F. Kahlbaum Chemische Fabrik, Adlershof bei Berlin, Germany) were joined together in a skin-dried sand mold to make one sample, by pouring molten antimony (from same source) at the point of joining.	[f] 99.9+	[g] 6.656
1451	19×7	Pieces of cast antimony from same source as sample 1450 were melted in a graphite crucible, open flame, and cast in a skin-dried sand mold.	[f] 99.9+	[g] 6.684

[a] The length of each sample was about 300 mm.
[b] After the thermal expansion determinations were completed, chemical analyses were made on pieces cut from the ends and the center of each sample.
[c] Density determinations were made on pieces cut from the samples after the thermal expansion measurements had been completed.
[d] Lead not detected. Chemical analysis made by H. A. Buchheit, formerly of this Bureau.
[e] Determined by Miss E. E. Hill, formerly of this Bureau.
[f] Lead, iron, copper, and zinc were not detected in a ten-gram sample. Chemical analysis made by W. D. Mogerman of this Bureau.
[g] Determined by E. L. Peffer of this Bureau.

After the determinations on the thermal expansion of the samples of polycrystalline antimony had been completed, microscopic examinations of portions from samples 1067 and 1450 were made.[33]

Sample 1067 showed only one kind of surface of fracture, which was coarsely granular and columnar in appearance. Sample 1450 displayed two different surfaces of fracture. One of these was a coarse grained fracture in which the grains were apparently columnar. The other fracture appeared to be fine grained and not markedly columnar. This suggested a variation in structure along the length of the sample, which was later confirmed by microscopic examination.

For microscopic examination three cross sections were cut from sample 1067. Two of these sections are shown at the left in figure 4. Eight cross sections were cut from specimen 1450. Three of these sections are shown at the right in figure 4 and four sections are shown in figure 5.

Figure 4 shows the structure of sample 1067 to be markedly columnar and uniform along the length of the sample. Figure 6 shows the area at A, figure 4, at a higher magnification. Near the edge (top of figure) there are a number of comparatively small grains, all apparently columnar. This was probably a region of rapid cooling due to the chilling effect of the mold in casting. Farther from the edge in a region of less rapid cooling the grains are larger and their columnar nature more pronounced. These grains, particularly the large ones in which growth was less restricted, show cleavage planes perpendicular to the axes of the columns. These are shown at a higher magnification in figure 7. It will be noted that the cleavage planes are mostly in the same direction. Many of them pass from one grain to another with little change in direction. Only in small grains, where crystalline growth was probably restricted, are there marked differences in the direction of the cleavage planes.

Antimony crystallizes in the rhombohedral form (hexagonal system) and has a perfect cleavage parallel to the basal plane of the

[33] By D. J. McAdam, Jr., and R. E. Pollard of this Bureau.

hexagonal system. It is probable that the cleavage planes shown in figure 7 are parallel to the basal planes. Their similarity indicates a preferred orientation in sample 1067.[34] It is probable that each of the columnar grains growing toward the center approximates a single crystal.

It will be noted from figures 4 and 5 that the structure of sample 1450 varies considerably along its length. Some of the cross sections shown in these figures are coarse grained and markedly columnar in structure. Others are fine grained and columnar only at or near the edges. It is estimated that between one-half and two-thirds of this material was fine grained and not markedly columnar. Figures 8 and 9 show the differences in structure in different sections of this material. These figures show, respectively, the areas at B and C of figure 5. In figure 8 the columnar structure is marked. In figure 9 the columnar structure is marked only at the edge (top of figure). In the interior the grains are almost entirely equiaxed.

Figure 10 shows the structure of a markedly columnar section of sample 1450 at a higher magnification. In this material the cleavage planes are diversified in direction. Even in markedly columnar sections there is much less evidence of a preferred direction of cleavage than in sample 1067.

It seems probable that in such regions relatively few crystals grew without restriction, in the direction of the radial temperature gradient, and that the rest of the material solidified between these columnar crystals so as to have a pseudomorphic columnar structure. It appears probable that when antimony crystals grow freely in the direction of a steep temperature gradient, the column elongates in the direction of the principal axis, the axis along which the coefficient of expansion is greatest.

In noncolumnar sections there is no evidence of preferred direction of cleavage. Sample 1450,[35] therefore, shows evidence of preferred orientation in only a small proportion of its length and cross section.

The results obtained on the microscopic examination of these samples may be summarized as follows:

Sample 1067 was found to be uniformly cross grained and columnar. The structure was uniform along the length of the sample. In this material the cleavage planes displayed a markedly preferred direction perpendicular to the axis of the columns.

The structure of sample 1450 was found to vary considerably along its length. Part of this material was coarse grained and columnar. In other parts the structure was fine grained and not columnar. Even in the columnar portions this material did not show as much evidence of preferred orientation as did sample 1067. In sections which were not columnar no evidence of preferred orientation was found.

The large differences of density (shown in table 8A) between the three samples of polycrystalline antimony are doubtless to be explained by the formation of microscopic cavities, on account of unequal contraction in different directions of the crystal grains in cooling from

[34] The thermal expansion of such material is expected to vary considerably, depending on the direction in which it is measured. Measured longitudinally (across the columns) the thermal expansion would be expected to approximate that of a single crystal perpendicular to the axis. It is significant that the coefficient of expansion of 9×10^{-6} (20 to 100° C) found for sample 1067 (table 10) is near that of 8×10^{-6} given for a single crystal perpendicular to the axis (table 6).

[35] It is significant that the coefficient of expansion (20 to 100° C) found for this sample (table 10) is practically equal to the value 11.1×10^{-6} computed for polycrystalline antimony having random orientation (page 542).

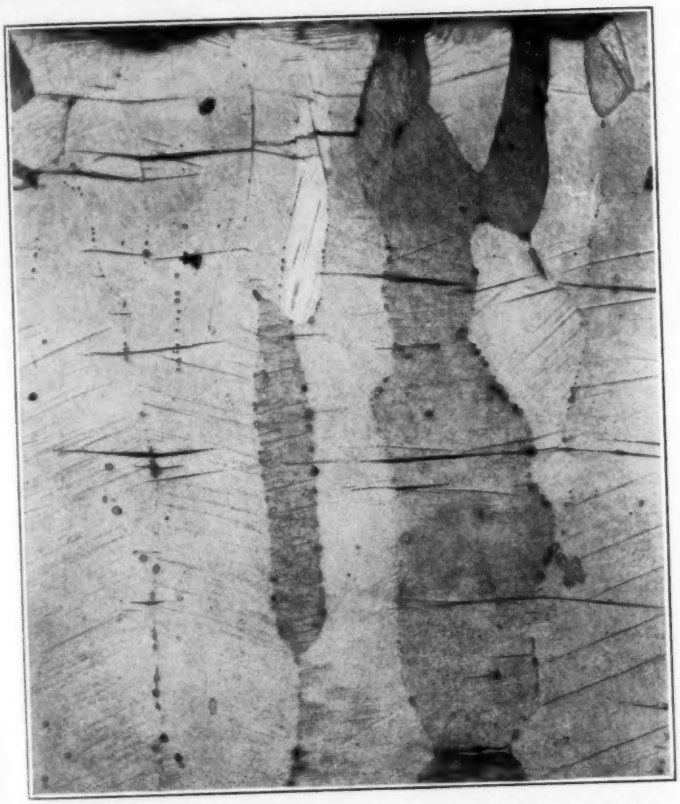

FIGURE 7.—*Structure of sample 1067 showing preferred direction of cleavage planes.*

Edge of sample at top of figure. Electrolytic etch in 5 percent oxalic acid. ×100.

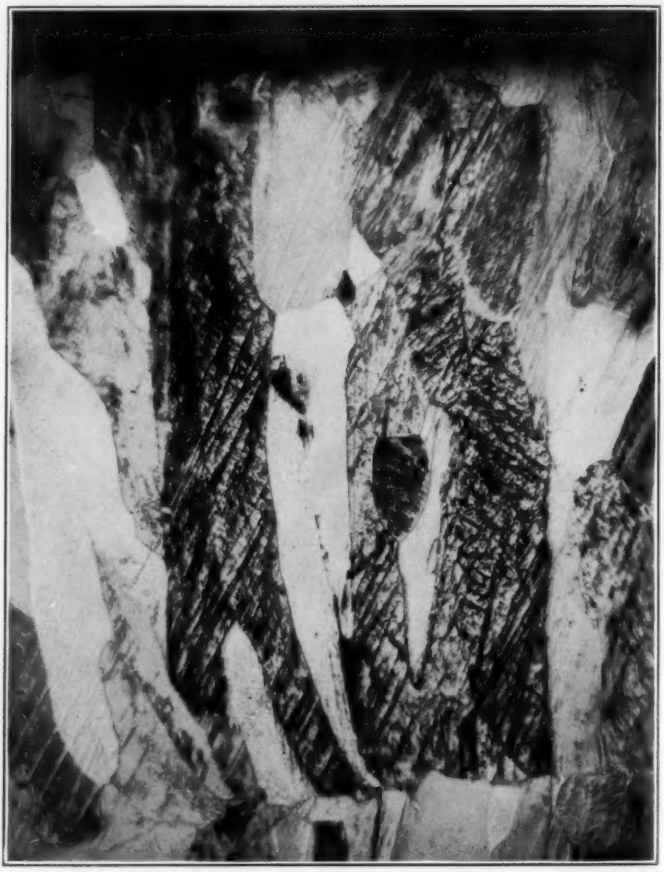

FIGURE 8.—*Area at* B, *figure 5, showing columnar structure of portion of sample 1450.*

Edge of sample at top, center of sample at bottom of figure. Electrolytic etch in 5 percent oxalic acid. ×30.

FIGURE 9.—*Area at* C, *figure 5, showing noncolumnar structure of portion of sample 1450.*

Top of sample at top, center at bottom of figure. Electrolytic etch in 5 percent oxalic acid. ×30.

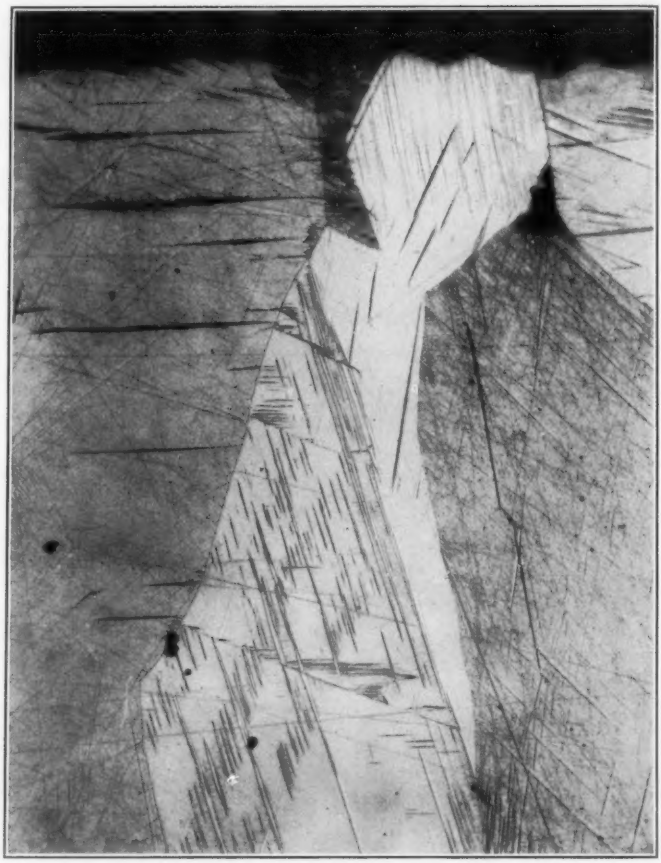

FIGURE 10.—*Structure of columnar portion of sample 1450, showing more diversified direction of cleavage planes.*

Edge of sample at top of figure. Electrolytic etch in 5 percent oxalic acid. ×100.

the melting point. The cavitation is different, for the mean orientation of each sample is not the same.

2. APPARATUS

The furnace shown in figure 1 of BS Scientific Paper S488 was used for the measurements of the linear thermal expansion of sample 1067, and the white furnace shown at the extreme left of figure 1 of BS Scientific Paper S524 was used for samples 1450 and 1451. Figure 4 of the latter paper indicates the method used in mounting samples 1450 and 1451 in the furnace.

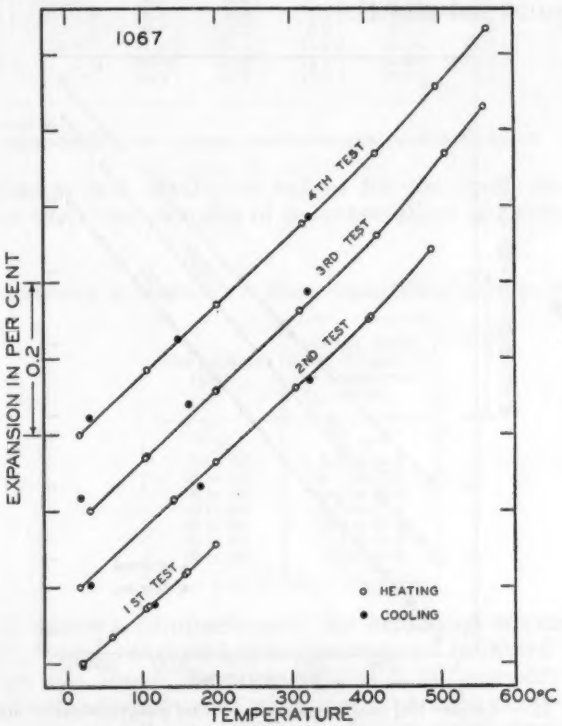

FIGURE 11.—*Linear thermal expansion of cast polycrystalline antimony.*
[Sample 1067.]

Expansion measurements were made by means of micrometer microscopes, which were sighted on fine wires suspended from or in contact with the ends of the specimen. For a detailed description of the apparatus and the methods used, the reader should refer to the publications mentioned. The apparatus used for the determinations of the thermal expansion of polycrystalline antimony is more accurate than the apparatus employed for the measurements of the expansion of monocrystalline antimony.

3. RESULTS

Measurements [36] were made on the linear thermal expansion of three samples of cast polycrystalline antimony at various temperatures between 20 and 560° C. The results obtained are indicated in figures 11 and 12. The smoothness of the thermal expansion curves shows that there is no polymorphic transition [37] between 20 and 560°C. From X-ray examination of the crystal structure of antimony to 210° C, and from measurements on the electrical resistance between 20 and 550° C, and on the thermal expansion up to 600° C, Schulze and Graf [38] likewise concluded that antimony has no allotropic transformation between 20 and 600° C.

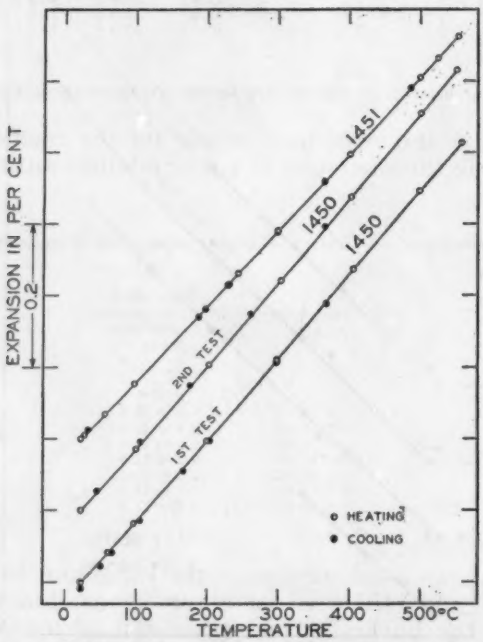

FIGURE 12.—*Linear thermal expansion of cast polycrystalline antimony.*
[Samples 1450 and 1451.]

Table 10 gives average coefficients of expansion which were derived from the expansion curves of figures 11 and 12. This table also indicates the difference in length before and after each expansion test. The plus (+) sign signifies an increase in length and the minus (−) sign a decrease in length.

[36] H. S. Krider assisted in the measurements on the thermal expansion of polycrystalline antimony. An abstract of these results was reported by Hidnert and Krider to the American Physical Society at the Chicago meeting in November 1932. See Phys. Rev. **42**, 911 (1932).

[37] Cohen and Van den Bosch, Z. Phys. Chem. **89**, 757 (1915); and Jaenecke, Z. physik. Chem. **90**, 337 (1915) reported transformations in antimony at 106° C and between 125 and 137° C, respectively. Kersten, Physics **2**, 276 (1932) reported that electrodeposited antimony has an amorphous structure when deposited at temperatures below 25° C, and changes from amorphous to crystalline between 25 and 30° C.

[38] Schulze and Graf, Metallwirtschaft, **12**, 19 (1933). These authors state that the irregularity found near 100° C in the electrical resistance of polycrystalline antimony before tempering or after tempering at 200° C, can apparently be explained by mechanical deformation and not by an allotropic transformation. They did not publish any quantitative data on the thermal expansion of antimony, for they were interested only in the shape of the expansion curve.

TABLE 10.—*Average coefficients of linear expansion of cast polycrystalline antimony*

Sample	Test no.	Average coefficients of expansion per degree centigrade							Change in length after heating to maximum [1] temperature and cooling to room temperature
		20 to 60° C	20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C	2 to 500° C	20 to 550° C	
		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
1067	1	8.5	8.4	8.7					−0.003
	2		9.8	9.3	9.2	9.2	9.5		−.010
	3		9.4	9.4	9.3	9.3	9.8	10.0	+.029
	4		9.3	9.3	9.2	9.3	9.6	9.7	+.009
1450	1	10.8	[2] 11.0	11.1	11.3	11.4	11.5	11.5	−.008
	2		10.9	11.3	11.4	11.5	11.6	11.6	.000
1451	1	10.2	10.2	10.4	10.5	10.5	10.6	10.6	+.002

[1] See figures 11 and 12.
[2] This value is approximately that computed later for complete random orientation.

The minimum and maximum values for the coefficients of linear expansion of the three samples of polycrystalline antimony are given in table 11.

TABLE 11.—*Summary of coefficients of linear expansion of polycrystalline antimony*

Temperature range	Average coefficients of expansion per degree centigrade
° C	× 10⁻⁶
20 to 60	8.5 to 10.8
20 to 100	8.4 to 11.0
20 to 200	8.7 to 11.3
20 to 300	9.2 to 11.4
20 to 400	9.2 to 11.5
20 to 500	9.5 to 11.6
20 to 550	9.7 to 11.6

Figure 13 shows a comparison of the expansion curves of samples 1067,[39] 1450,[40] and 1451 with the observations obtained by previous observers on the linear thermal expansion of monocrystalline and polycrystalline antimony, and with the expansion curves[41] of monocrystalline antimony (0° and 90° orientation only), from this paper. An examination of the results in table 10 and figure 13 shows that a different expansion was obtained for each sample of polycrystalline antimony used in the present investigation. The values obtained for the expansion of these samples of polycrystalline antimony are intermediate between those obtained for monocrystalline antimony having 0° and 90° orientation, respectively. The values for polycrystalline antimony are much closer to the values obtained for monocrystalline antimony of 90° orientation than for 0° orientation. It appears that the explanation is to be sought in the structure of the metal, for the expansion of crystalline antimony depends on its

[39] Curve obtained from four tests on heating.
[40] Curve obtained from two tests on heating.
[41] Obtained from the data given in table 6. The curve for 0° orientation represents extrapolated values, and was therefore drawn as a broken or dashed curve. This curve, computed from equations 1 to 4, which were derived from the expansion data for orientations between 32 and 90°, is in excellent agreement with the data reported by Fizeau and Bridgman (see fig. 13).

orientation. Assuming that there is random orientation[42] of the crystals in a bar of polycrystalline antimony, then the coefficient of linear expansion of polycrystalline antimony may be expressed by the following equation:

$$a=\frac{1}{3}(a_0+2a_{90}) \tag{6}$$

where a is the coefficient of linear expansion of polycrystalline antimony, a_0 is the coefficient of linear expansion of monocrystalline antimony having 0° orientation, and a_{90} is the coefficient of linear expan-

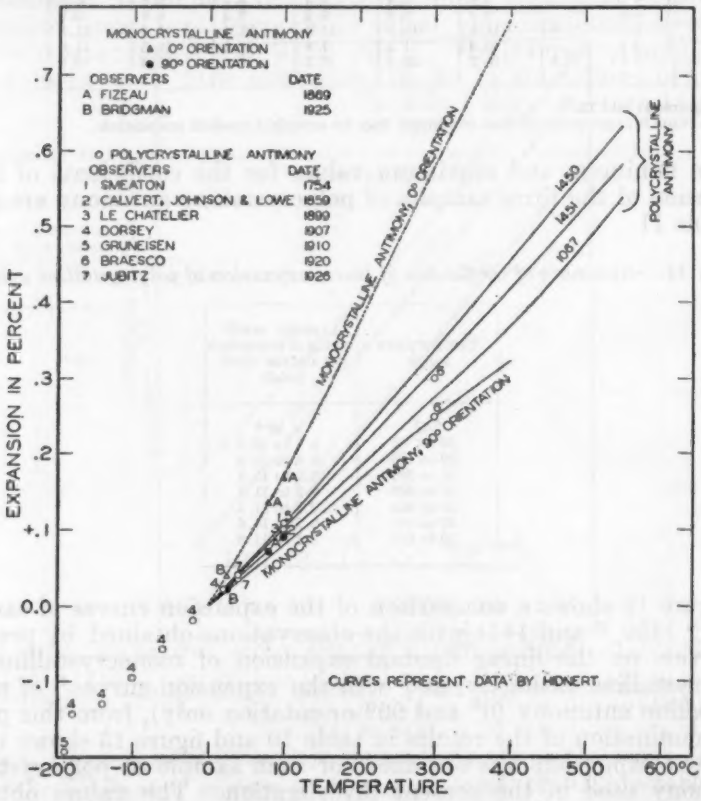

FIGURE 13.—*Comparison of linear thermal expansion of monocrystalline and polycrystalline antimony.*

sion of monocrystalline antimony having 90° orientation. If the values 17.2×10^{-6} and 8.0×10^{-6} (table 6) are substituted for a_0 and a_{90}, respectively, in equation 6, the value[43] 11.1×10^{-6} is obtained for the coefficient of linear expansion of polycrystalline antimony (random distribution) between 20 and 100° C. Values different from this may be considered as due to variations from random orientation.

[42] Gough, Am. Soc. Testing Materials **33**, part 2, (1933), pointed out that metals in the normal state usually consist of an aggregate of very small crystals of random orientation, this structure being due to crystallization from the liquid proceeding simultaneously from a number of different nuclei.

[43] This value can also be derived by taking one-third of the coefficient of cubical expansion of antimony (monocrystalline or polycrystalline).

The values of this paper apply only to cast antimony. Jubitz [44] found that a drawn sample of antimony [45] expands less than a sample as cast, and stated that this metal shows a distinct thermal anisotropy. He found larger differences for zinc and cadmium. He stated that working (rolling, hammering, drawing, etc.) metals [46] belonging to the regular system, has no appreciable effect on the expansivity, but that there is an effect on metals [47] which do not belong to the regular system. Braesco [48] observed that a quenched or annealed sample of agglomerated antimony expands less than a quenched or annealed sample of cast antimony.

By means of equation 5, coefficients of cubical expansion of antimony were computed from the coefficients of linear expansion of monocrystalline antimony (table 6) obtained by Fizeau, Bridgman, and Hidnert, respectively. Table 12 shows a comparison of the computed coefficients of cubical expansion with those observed by Kopp, Matthiessen, and Lussana.

TABLE 12.—*Comparison of observed and computed coefficients of cubical expansion of antimony*

Observer	Temperature range	Coefficients of cubical expansion per degree centigrade	
		Observed	Computed [1]
	°C	$\times 10^{-6}$	$\times 10^{-6}$
Kopp	12 to 42	33	
Matthiessen	0 to 100	31.7	
Lussana	9 to 72	35.3	
Fizeau	0 to 100		34.8
Bridgman	15 to 25		31.6
Hidnert	20 to 100		33.2
Average		33.3	33.2

[1] From equation 5.

IV. CONCLUSIONS

1. MONOCRYSTALLINE ANTIMONY

1. The data obtained on the linear thermal expansion of the single crystals of antimony in the first heating and cooling indicate that they were produced in a state of strain. Davey, in 1927, stated that all crystals are produced in a state of strain.

2. In most cases, the coefficients of linear expansion of the single crystals are higher in the second tests on heating than in the first tests on heating.

3. The following equations show the relationships between the coefficients of expansion and the orientations of the single crystals of antimony:

$$_{20}E_{100}=(17.17-0.1951\theta+0.001039\theta^2)10^{-6} \quad (1)$$

$$_{20}E_{200}=(18.88-0.2440\theta+0.001411\theta^2)10^{-6} \quad (2)$$

$$_{20}E_{300}=(19.54-0.2579\theta+0.001479\theta^2)10^{-6} \quad (3)$$

$$_{20}E_{400}=(19.49-0.2548\theta+0.001430\theta^2)10^{-6} \quad (4)$$

[44] See table 2.
[45] Also for bismuth.
[46] Bronze and cast iron.
[47] Antimony, zinc, cadmium, and magnesium.
[48] See table 2.

In these equations, ${}_{20}E_{100}$, ${}_{20}E_{200}$, ${}_{20}E_{300}$ and ${}_{20}E_{400}$ represent the average coefficients of linear expansion from 20 to 100° C, 20 to 200° C, 20 to 300° C, and 20 to 400° C, respectively, and θ represents the orientations of the single crystals between 32 and 90°. The probable errors of ${}_{20}E_{100}$, ${}_{20}E_{200}$, ${}_{20}E_{300}$, and ${}_{20}E_{400}$ are $\pm 0.4\times10^{-6}$, $\pm 0.4\times10^{-6}$, $\pm 0.3\times10^{-6}$, and $\pm 0.3\times10^{-6}$, respectively. The computed values for the average coefficients of expansion of monocrystalline antimony with 0° orientation and 90° orientation are 17.2×10^{-6} and 8.0×10^{-6}, respectively, between 20 and 100° C.

4. The coefficient of linear expansion depends upon the direction taken. Figure 3 and table 6 show the coefficients of expansion for various orientations. The coefficients of expansion along the trigonal axis (0° orientation) are about twice as large as the coefficients of expansion along a direction perpendicular to this axis (90° orientation). These results confirm Bridgman's statement that the atoms are connected more loosely across the cleavage plane, so that external forces produce greater effects perpendicular to this direction (along trigonal axis) than in others.

2. POLYCRYSTALLINE ANTIMONY

1. The linear thermal expansion curves of polycrystalline antimony show that there is no polymorphic transition between 20 and 560° C.

2. The average coefficients of linear expansion of three samples of polycrystalline antimony for various temperature intervals between 20 and 550° C were found to range from 8.4×10^{-6} to 11.6×10^{-6} per degree C. The cause of the differences obtained in the expansion of different samples of polycrystalline antimony is attributed to variations in the average orientation of the crystals.

3. Figure 13 shows a comparison of the linear thermal expansion of monocrystalline and polycrystalline antimony.

The author expresses his appreciation to Prof. P. W. Bridgman of Harvard University for his cooperation in the work on single crystals of antimony. Acknowledgment is also due to Dr. S. B. Hendricks of the Bureau of Chemistry and Soils of the U. S. Department of Agriculture, and to the following members of the staff of the National Bureau of Standards: L. J. Briggs, H. W. Bearce, W. Souder, M. R. Thompson, and L. V. Judson, for valuable suggestions.

WASHINGTON, December 20, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP785

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A FILTER FOR OBTAINING LIGHT AT WAVE LENGTH 560 mμ *

By Kasson S. Gibson

ABSTRACT

A filter transmitting a narrow band of light at 560 mμ is of particular importance in the colorimetry of sugar solutions, in optical pyrometry, in abridged spectrophotometry, and in photometry. A new 4-component glass filter has been designed, which isolates and transmits light at 560 mμ more effectively than previous filters. Two components of this filter are of Corning glass and two of Jena glass.

The spectral transmissions of the filter and its components are illustrated. The spectral centroid of the light transmitted by the filter is at 560 mμ for both incandescent and daylight illuminants. Various other luminous characteristics of the filter are also defined and values given.

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I. INTRODUCTION

The wave length 560 mμ has been shown to have particular significance in the colorimetry of sugar solutions.[1] "Through a simple measurement of absorption or transmission at this wave length, it is possible to arrive at a nearly correct estimate of color in relation to the effective quantity of coloring material per gram of saccharine dry substance.[2]" Values at this wave length may be obtained either (1) by means of a spectrophotometer with the usual incandescent illuminant, (2) by use of the Hg-vapor illuminant, measurements being made at 546 and 578 mμ, and the value at 560 mμ being derived from the values obtained at the two Hg wave lengths,[3] or (3) with a photometer, incandescent illuminant, and filter properly isolating a narrow spectral region at 560 mμ.[4] The last method is the simplest

* This paper will appear also in J. Optical Soc. Am. **25**, 131 (1935).

[1] H. H. Peters and F. P. Phelps, Color in the sugar industry. Tech. Pap. BS **21**, 261(1926-27) T338; H. H. Peters and F. P. Phelps, A technical method of using the mercury arc to obtain data at wave length 550 mμ in the spectrophotometric analysis of sugar products. BS J. Research **2**, 335 (1929) RP38.
J. F. Brewster, Color filter for visual sugar colorimetry. Facts About Sugar **28**, 228 (1933).

[2] RP38, page 335; (see footnote 1).

[3] RP38 (see footnote 1).

[4] As proposed by Brewster (see footnote 1).

but depends for its reliability on the effectiveness of the filter used to obtain this wave length.

A filter transmitting only a narrow spectral region in the green or yellow-green is also of use in certain problems in optical pyrometry. Such a filter has been used (1) in the determination of the true temperature and total radiation of luminous gas flames,[5] and (2) in checking the accuracy with which the temperature scale can be realized in practice.[6] In these cases, the exact location of the isolated region is unimportant, although, of course, it must be accurately known; 560 mμ is as suitable as any other wave length. The quantity determined and used in such work is known as the "effective wave length";[7] and in order that this be as independent as possible of the visibility function, which varies from one observer to another, the filter must isolate a very narrow spectral region. The filter should, however, transmit as freely as possible in this region in order that sufficient light be available for measurement.

A third use for a 560 mμ filter is in abridged spectrophotometry. For certain types of work complete spectrophotometry is unnecessary; it has been found sufficient to use a photometer with filters [8] for isolating the four principal Hg lines and such additional spectral regions as may be desirable and are obtainable with an incandescent illuminant. A 560 mμ filter gives a point well spaced between the green and yellow lines of Hg.

Such a filter is also desired in certain photometric investigations.[9] The filter would furthermore be useful wherever "cold light" is desired, since the transmitted energy is so close to the spectral region of maximum visibility.

The present filter was made possible by the appearance of two new Jena glasses, described below. It was designed and constructed during the summer of 1934,[10] and was described at the October 1934 meeting of the Optical Society of America.[11]

II. SPECTRAL TRANSMISSION OF THE FILTER AND ITS COMPONENTS

The following glasses were used in combination, with thicknesses as noted: 1. Corning [12] 351, 4.55 mm; 2. Corning didymium, 5.82 mm; 3. Jena [13] VG 3, 1.99 mm; 4. Jena BG 18, 1.94 mm.

[5] H. C. Hottel and F. P. Broughton, Determination of true temperature and total radiation from luminous gas flames—Use of special two-color optical pyrometer. Ind. Eng. Chem. Anal. Ed., **4**, 166 (1932).

[6] H. T. Wensel, National Bureau of Standards, unpublished work.

[7] P. D. Foote, "Center of gravity" and "Effective wave length" of transmission of pyrometer color screens, and the extrapolation of the high-temperature scale. Bul. BS **12**, 483 (1915–16) S260.

[8] W. D. Appel, A method for measuring the color of textiles., Am. Dyestuff Reptr. **17**, 49 (1928); Genevieve Becker and W. D. Appel, Evaluation of manila rope fibers for color. BS J. Research **11**, 811 (1933) RP627

[9] Robert Livingston, Note on the transmission characteristics of four green glass filters. J. Optical Soc. Am. **24**, 227 (1934).

[10] The author was not at that time aware of the work of Livingston, who used three of the four components of the present filter in one of the filters designed by him.

[11] J. Optical Soc. Am. **25**, 46 (1935).

[12] For Corning glasses see advertising booklet entitled, Glass Color Filters, issued by Corning Glass Works, Corning, N. Y.

[13] For Jena glasses see advertising booklet entitled, Jena Colored Optical Filter Glasses for Scientific and Technical Purposes, issued by Jena Glass Works, Schott and Gen., Jena, and obtainable from Fish-Schurman Corporation, 230 East Forty-fifth Street, New York, N. Y.

The spectral transmissions of these glasses were determined for the thicknesses given and are illustrated in figure 1. In this figure is

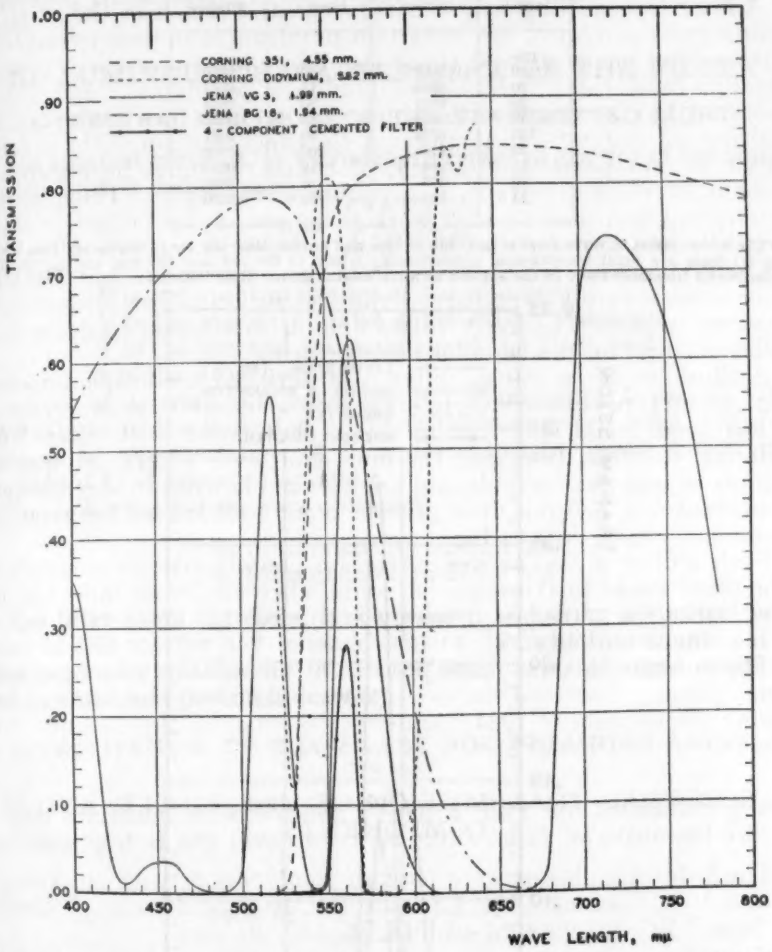

FIGURE 1.—*Spectral transmissions of the component glasses and the cemented filter.*
The curve for the didymium glass would be of the usual type beyond the range shown.

also shown the measured spectral transmission of the combination of four glasses, cemented together with canada balsam; these values are taken from table 1.

TABLE 1.—*Spectral transmission of 560 mμ filter*

Wave length	Transmission	Wave length	Transmission
mμ		mμ	
510	[a]0.0000	570	.0095
20	.0004	75	.0003
30	.0011	80	.0004
40	.0019	85	.0001
545	.0029	90	.0001
50	.028	600	.0006
55	.174	10	.0003
60	.275	20	.0001
65	.212	30	[a].0000

[a] The transmission at wave lengths less than 510 mμ and greater than 630 mμ is effectively zero, except that (1) there is a slight transmission, approximately 0.0002, in the red near 690 mμ, and (2) the filter undoubtedly transmits freely in the infrared at wave lengths greater than 1500 mμ.

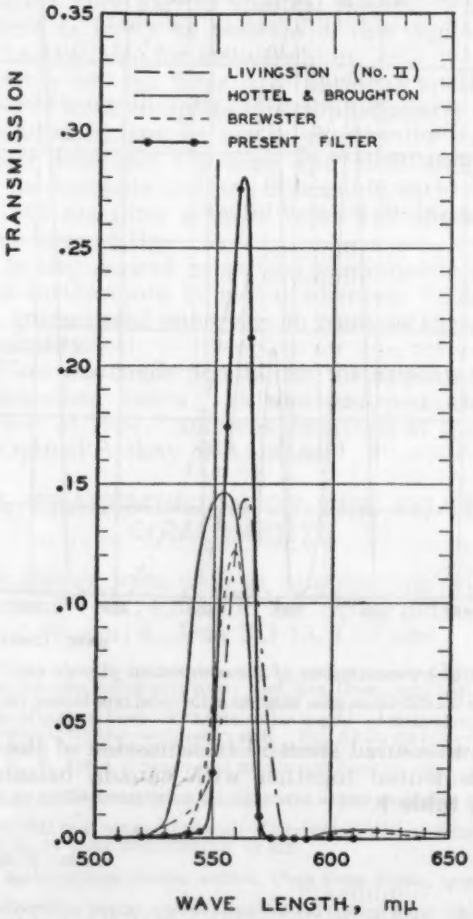

FIGURE 2.—*Comparison of spectral transmission of present filter with others of similar type.*

gure 2 is shown the present filter, compared with other filters [14] designed to obtain the same or closely adjacent regions. It may be

[14] The values for Livingston's filter have been multiplied by $(1/.91)^2$ to make them more nearly comparable to the other data. His published curve refers to an uncemented 4-component filter.

noted that the spectral transmission curve of the present filter has a ratio of height to width about twice that of the other filters. The decreased transmission in the region 590 to 650 mμ is also of importance.

III. LUMINOUS CHARACTERISTICS OF THE FILTER

1. SPECTRAL CENTROID OF THE TRANSMITTED LIGHT

The spectral centroid, or wave-length center of gravity of the transmitted light, is defined as:[15]

$$\lambda_c \equiv \frac{\int_0^\infty EVT\lambda d\lambda}{\int_0^\infty EVTd\lambda}$$

in which

E is the spectral energy of the illuminant,
V is the visibility for an equal-energy spectrum,
T is the spectral transmission of the filter, and
λ is the wave length.

Values of λ_c were computed for ICI illuminants A and C[16] by summations of the indicated products taken at every 5 mμ. Illuminant A is representative of incandescent light (near 2,840° K), illuminant C of average daylight.

The following values were obtained:

$$\lambda_c \text{ (illuminant A)} = 560.0 \text{ m}\mu$$
$$\lambda_c \text{ (illuminant C)} = 559.8 \text{ m}\mu$$

The filter may, therefore, be considered as having a spectral centroid of 560 mμ for any incandescent or daylight illuminant. It is thus especially suitable for use in the colorimetry of sugar solutions and in abridged spectrophotometry.

2. EFFECTIVENESS OF THE FILTER FOR OBTAINING LIGHT AT 560 mμ

The combined effectiveness, $F_{\lambda'}$, of a filter for transmitting and isolating light at any given wave length, λ', may be expressed as

$$F_{\lambda'} \equiv T_{\lambda'} - \frac{\Sigma_0^\infty EV \mid \lambda - \lambda' \mid T\Delta\lambda}{\Sigma_0^\infty EV \mid \lambda - \lambda' \mid \Delta\lambda}$$

where the symbols have the same meanings as above and the absolute value signs ($\mid \mid$) indicate that the differences are to be taken all greater than zero. For the present filter, we take $\lambda' = \lambda_c = 560$ mμ and $T_{\lambda_c} = 0.275$.

Values of $F_{\lambda c}$ were computed for ICI illuminants A and C by taking summations of the indicated products at every 5 mμ. The following values were obtained:

$$F_{\lambda c} \text{ (illuminant A)} = 0.275 - 0.003 = 0.272$$
$$F_{\lambda c} \text{ (illuminant C)} = 0.275 - 0.004 = 0.271$$

[15] P. D. Foote, Bul. BS 12, 483 (1915-16) S260.
[16] Int. Comm. Illum. Proc. pages 22 and 23 (1931). ICI standard values of V were also used.

The effectiveness of the other filters illustrated in figure 2 is much less than this. For example, the Hottel and Broughton filter has an effectiveness

$$F_{\lambda'}=0.146-0.009=0.137$$

for illuminant A with λ' taken at 555 mμ, which is close to the value of λ_e for this filter. For Livingston's filter $F_{\lambda e}$ will equal 0.14 approximately, and for Brewster's filter 0.12 approximately; this is apparent by inspection, since for filters of the type illustrated in figure 2 the value of $F_{\lambda e}$ is slightly less than the maximum transmission.

3. EFFECTIVE WAVE LENGTH FOR OPTICAL PYROMETRY

Within the visible spectrum, the energy distribution of a black body is represented closely by Wien's equation

$$E=C_1\lambda^{-5}e^{-\frac{C_2}{\lambda\theta}} \tag{1}$$

If E_1 and E_0 represent the spectral-energy distributions of a black body at the respective temperatures, θ_1 and θ_0, the ratio of E_1 to E_0 may be written as

$$E_1/E_0=e^{\frac{C_2}{\lambda}\left(\frac{1}{\theta_0}-\frac{1}{\theta_1}\right)} \tag{2}$$

For two given temperatures the value of the ratio is, therefore, simply a function of λ.

If V be the value of the visibility function at any wave length, λ, then

$$\frac{E_1V}{E_0V}=\frac{L_1}{L_0}=e^{\frac{C_2}{\lambda}\left(\frac{1}{\theta_0}-\frac{1}{\theta_1}\right)} \tag{3}$$

This is the principle of the optical pyrometer; by measuring the ratio of luminosities, L_1/L_0, for some known wave length, λ, the value of θ_1 may be computed from that of θ_0.

The type of optical pyrometer commonly employed does not, however, use light of a definite wave length, λ, but of a range of wave lengths transmitted by a suitable filter. The ratio of luminosities, R_L, measured with the pyrometer is in this case given by

$$R_L=\frac{\int_0^\infty E_1VTd\lambda}{\int_0^\infty E_0VTd\lambda} \tag{4}$$

where T is the spectral transmission of the filter used.

R_L may also be computed from this equation for any arbitrarily selected pair of temperatures, θ_1' and θ_0'. Substituting this computed value of R_L for E_1/E_0 in equation 2, or for L_1/L_0 in equation 3, and solving for λ, gives a wave length, λ_e, at which the ratio of spectral energies or luminosities is equal to the ratio of the luminosities which would be obtained with the filter for the two temperatures, θ_1' and θ_0'.[17] The quantity, λ_e, is called the effective wave length.

The computation of λ_e may be repeated for other pairs of temperatures. Since λ_e changes but slightly with changes in either θ_1' or θ_0', a

[17] This method of treatment is due to Hyde, Forsythe, and Cady, Astrophys. J. 42, 294 (1915).

comparatively small number of values of λ_e need to be calculated to determine λ_e as a function of the upper and lower temperatures with sufficient accuracy throughout the useful range of measurement.

It can also be shown [18] that if the quantity

$$\lambda_\theta \equiv \frac{\int_0^\infty E_\theta V T d\lambda}{\int_0^\infty E_\theta V T (1/\lambda)\, d\lambda}$$

is calculated for a series of temperatures, the value of λ_e for two temperatures, θ_1 and θ_0, is given by the equation

$$\frac{1}{\lambda_e} = \frac{1}{2}\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_0}\right)$$

The changes in λ_θ with temperature and observer depend primarily upon the width of the transmission band of the pyrometer filter. Such filters are often used by observers whose visibility function has never been determined, and in such cases the effective wave length used is that calculated for the ICI standard observer. It is a distinct advantage, therefore, to have a filter for which the effective wave length does not differ much for different observers. The quantity, λ_θ, for the present filter has been computed by Dr. H. T. Wensel,[19] by summation with wave-length intervals of 2.5 mμ. The following values were obtained for the ICI observer:

λ_{1336} (gold point) $= 560.5_7$ mμ
λ_{2046} (platinum point) $= 560.2_3$ mμ

Dr. Wensel has also calculated the values for that observer, otherwise normal, whose visibility differs most from the standard.[20] For this observer the values found are:

$\lambda_{1336} = 560.7_4$ mμ
$\lambda_{2046} = 560.4_1$ mμ

The difference of 0.3 mμ between values for the two selected temperatures and that of 0.2 mμ between the extreme and standard observer are approximately ⅛ and ⅕ of the respective differences for the red selenium glasses ordinarily used in optical pyrometers. The present filter, however, will have its greatest application at temperatures above 2,000° K, because in this range the rather low transmission of the filter is compensated by the increased brightness of the illuminant and accurate measurement becomes possible. It is estimated that temperature determinations can be made with this filter which will be uncertain by not more than 1 or 2° K, even though the observer's visibility is unknown and the effective wave length is assumed constant.

[18] P. D. Foote, Bul. BS 12, 483 (1915–16) S260. Foote, Fairchild, and Harrison, Pyrometric practice. Tech. Pap. BS 170, see p. 271 (1921).
[19] The author is further indebted to Dr. Wensel for advice regarding the preparation of this section.
[20] Out of the 52 observers tested. See BS Sci. Pap. 19, 131 (1923–24) S475.

4. LUMINOUS TRANSMISSION

Luminous transmission is defined as

$$T_L \equiv \frac{\int^{\infty} VETd\lambda}{\int_0^{\infty} VEd\lambda}$$

Values of T_L were computed by summations of the indicated products taken at every 5 mμ.

For ICI illuminant A, $T_L=0.033$; for ICI illuminant C, $T_L=0.035$.

5. LUMINOUS EFFICIENCY OF THE TRANSMITTED ENERGY

Light is most efficiently produced by radiant energy at 555 mμ, the wave length of maximum visibility. At this wave length, the luminous efficiency is equal to the reciprocal of the least mechanical equivalent of light, M, the latest value for which is 0.001602 watt [21] per lumen. At any other wave length, the luminous efficiency is equal to V/M.

The luminous efficiency of the light transmitted by the filter is, therefore, equal to

$$e_L=\frac{\int_0^{\infty} ET(V/M)d\lambda}{\int_0^{\infty} ETd\lambda}=\frac{1}{M}\frac{\int_0^{\infty} ETVd\lambda}{\int_0^{\infty} ETd\lambda}$$

=616 lumens per watt for both ICI illuminant A and ICI illuminant C.

This value is about 99 percent of the maximum possible luminous efficiency, which is equal to 1/0.001602, or 624.2 lumens per watt. To make this value truly effective for the present filter, however, it must be used in combination with a water cell of sufficient thickness [22] to absorb the infrared energy otherwise transmitted by the filter.

IV. REPRODUCIBILITY AND PERMANENCE

It is well known that glasses of the type used in this filter are not precisely reproducible in spectral transmission from one melt to another. In this case, however, it is believed that little difficulty will be experienced in securing a satisfactory duplication of the present filter if the component parts are ordered by number and thickness from the respective dealers. A few hundredths of a millimeter deviation from the thicknesses given is of little consequence. The exact location of the transmitted light depends mostly on the Corning didymium and Jena VG 3 glasses, and by decreasing the thickness of one or the other of these glasses if necessary, the transmission band can be shifted slightly towards longer or shorter wave lengths. The other two glasses contribute little towards defining the exact position of this band, but are important in preventing the transmission of light at longer and shorter wave lengths.

Most glasses are considered permanent with ordinary usage. The surface of the Jena VG 3 glass tends to deteriorate somewhat upon ordinary exposure. It should, therefore, be mounted on the inside of the filter.

WASHINGTON, MARCH 1, 1935.

[21] Wensel, Roeser, Barbrow, and Caldwell, J. Research NBS 13, 161 (1934) RP699.

[22] From the published data on the Jena BG 18 glass (see footnote 13), it is estimated that 2 cm of water are sufficient to give complete absorption of infrared energy with the present filter.

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RESEARCH PAPER RP786

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REFRACTIVE INDEX OF RUBBER

By Archibald T. McPherson and Arthur D. Cummings

ABSTRACT

The refractive index of rubber was measured on an Abbe refractometer by a method of total reflection. For plantation Hevea rubber and purified rubber average values of n_D^{25} are 1. 5188 and 1. 5190, respectively. The index of crude rubber is not altered by the introduction of insoluble fillers. Sulphur in solution increases n_D^{25} of crude rubber by 0. 0016 for each percent, and phenyl-β-naphthylamine, by 0. 0015 for each percent. The refractive index of vulcanized compounds of purified rubber and sulphur is given by,

$$n_D^t = 1.5190 + 0.00370\ S_c - 0.00035\ (t-25)$$

where S_c represents the percentage of combined sulphur, between 0 and 16, and t, the temperature in degrees centigrade, between 10 and 75° C. The curve relating refractive index to temperature for a compound containing 19 percent of sulphur undergoes a change in slope at about 17° C. Preliminary measurements on compounds containing 19 to 32 percent of sulphur indicate that the transition from soft to hard rubber is accompanied by a decrease in the slope of the curve relating refractive index to temperature.

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I. INTRODUCTION

This paper presents an exploratory study of the refractive index of rubber. Previous observations on the refractive index of rubber have been, for the most part, restricted to transparent samples.[1] In the present investigation, however, by using reflected light rather than light at grazing incidence, it was found possible to extend the range of measurements to rubber samples that were somewhat dark in color or that were very nearly opaque. Such being the case, determinations of refractive index were made not only on translucent

[1] References to several previous publications on the refractive index of rubber are given in two papers by Kirchhof, Kautschuk 8, 137 (1932), and 9, 172 (1933); English translations, Rubber Chem. Tech. 6, 92 (1933) and 7, 608 (1934). Other publications on the refractive index of rubber are: Ayrton and Perry (and Jellett) Phil. Mag. [5], 12, 196 (1881); Gladstone and Hibbert, J. Chem. Soc. Trans. 53, 680 (1888); Curtis and McPherson, Tech. Pap. BS 19, 698 (1925) T299; Tanaka, Trans. Inst. Rubber Ind. 2, 330 (1927); and Shacklock, Trans. Inst. Rubber Ind. 7, 354 (1932). Preliminary mention of the present work was made in BS Tech. News Bul. 194, p. 66 (June 1933).

samples of unvulcanized or soft vulcanized rubber, but also on binary mixtures of rubber and different compounding materials, and on compounds of rubber and sulphur containing 0 to 19 percent of sulphur and covering the range from soft to semihard rubber.

Different samples of unvulcanized Hevea rubber, of plantation origin, all showed approximately the same refractive index, irrespective of considerable variations in the nonhydrocarbon constituents. The index was not appreciably altered by the amount of mastication which rubber ordinarily receives in processing and mixing with compounding ingredients. Mixtures of rubber with substances insoluble in it showed the same index as the rubber itself, while mixtures with soluble substances differed in index from rubber by an amount which depended upon the index of the substance and the amount in solution. Measurements of refractive index, therefore, afford a means of measuring the solubility of substances in rubber and were employed for determinations of the solubility of sulphur and of a common antioxidant, phenyl-β-naphthylamine.

Sulphur in combination with rubber had a relatively greater effect on the refractive index than did sulphur in solution. For vulcanized rubber-sulphur compounds in the soft-rubber range the refractive index was a simple linear function of the percentage of sulphur and also of the temperature. Preliminary measurements on vulcanized compounds in the hard-rubber range indicate that the change in physical properties of rubber-sulphur compounds from soft to hard was accompanied by a decrease in the slope of the curve relating refractive index to temperature.

II. METHOD OF MEASURING REFRACTIVE INDEX OF RUBBER

The measurements of refractive index were made on critical-angle refractometers of the Abbe type, but the border-line characteristic of rubber was obtained by using reflected light rather than light at grazing incidence. Two instruments were used. One was designed for this type of measurement, but it had the practical limitation that the prism was not jacketed to permit the circulation of water for temperature control. This instrument was used in a constant-temperature room at approximately 25° C. In order to make observations over a range of temperature a standard Abbe refractometer having a water-jacketed prism was employed. Since there was no provision for admitting light into the prism from the face opposite the one on which the specimen was mounted, a slab of plane-parallel glass having ground edges was interposed between the specimen and the prism. Light was introduced through the edge of this slab, as illustrated in figure 1. The illuminating prism was, of course, removed. The specimen and glass slab were enclosed on three sides by a cored metal housing. The control of temperature was secured by circulating water through this housing and the jacket around the prism. The glass slab had a refractive index of 1.65, which was significantly higher than that of the rubber, as required by the optical system. α-Bromonaphthalene was employed to obtain optical contact between the glass slab and the prism.

Samples of rubber for measurement were mounted on the prism of the refractometer or on the glass slab without employing a contact

liquid. No difficulty was experienced in obtaining good optical contact between soft rubber and glass, provided the surface of the rubber was clean and smooth. This condition was met by molding the specimens between sheets of polished aluminum, and by removing the aluminum just before the rubber was to be attached to the glass. In preparing crude-rubber specimens, the rubber was milled until it ran smoothly on the rolls, compounding ingredients, if any, were added quickly, and the resultant batch was pressed out between thin aluminum sheets in a vulcanizing press at about 100° C. Vulcanized specimens were cured between the aluminum sheets.

Samples of hard or semihard rubber did not give good contact when pressed against glass at room temperature. These were prepared in sheets about 0.25 mm in thickness and were mounted on the

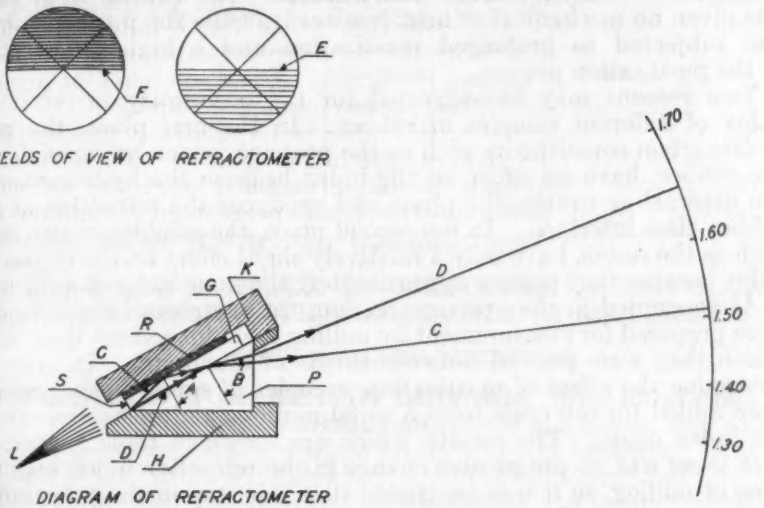

FIGURE 1.—*Optical system for the measurement of refractive index.*

R, rubber sample; G, plane parallel glass slab with fine ground edge toward light source; P, refractometer prism; L, light source; A, critical angle characteristic of rubber; B, critical angle characteristic of glass slab; C, limiting emergent ray for rubber; D, limiting emergent ray for glass slab; E, critical edge or border line characteristic of rubber; F, critical edge or border line characteristic of glass slab; H, metal housing cored for circulation of water.

glass slabs by pressing them together hot and allowing them to cool under pressure.

When measurements of refractive index are made by the method here employed the contrast between the two halves of the field, seen in the telescope of the refractometer, is not great. This contrast is diminished as the samples become darker in color or increase in opacity, and the boundary often becomes less distinct. This constitutes a limitation of the method, both as to the range of samples that can be employed and as to the precision of measurement.

III. REFRACTIVE INDEX OF UNVULCANIZED RUBBER

Several different samples of unvulcanized rubber, of plantation Hevea origin, were examined and all were found to possess approximately the same refractive index, irrespective of their hydrocarbon content or method of preparation. This is shown by the results

given in table 1. Two samples of rubber obtained by the evaporation of ammonia-preserved latex from different sources gave indices, n_D^{25}, of 1.5187 and 1.5192, respectively. Different samples of commercial smoked sheet and pale crepe gave indices from 1.5187 to 1.5189, with an average of 1.5188, while for purified rubber the index ranged from 1.5189 to 1.5191, with an average of 1.5190.[2] The various samples of unvulcanized rubber differed materially in composition and in the treatment which they were accorded in preparation. The latex rubber contained about 10 percent of resins, proteins, and soluble serum constituents, while the purified rubber contained about 0.5 percent of nonhydrocarbon constituents. The smoked sheet and pale crepe contained intermediate but not identical amounts of nonhydrocarbon constituents. The rubber from latex was given no mechanical or heat treatment, while the purified rubber was subjected to prolonged mastication and a high temperature in the purification process.

Two reasons may be suggested for the uniformity in refractive index of different samples of rubber. In the first place, the nonhydrocarbon constituents such as the proteins, which are insoluble in the rubber, have no effect on the index because the hydrocarbon is the external or continuous phase and produces the refraction at the rubber-glass interface. In the second place, the soluble constituents, such as the resins, have only a relatively slight effect on the refractive index because they possess approximately the same index as rubber.

As was noted in the previous section, the samples of crude rubber were prepared for measurement by milling them for a short time, after which they were pressed between sheets of aluminum. In order to determine the effect of mastication, samples of smoked sheet rubber were milled for intervals from 5 to 30 minutes and measurements of the index made. The results, which are shown in table 1, indicate that there was no progressive change in the refractive index with the time of milling, so it was concluded that this step in the preparation of the samples, as it was conducted in the present investigation, was without significant effect on the index.

TABLE 1.—*Refractive index of unvulcanized rubber*

Kind of rubber	Sample no.	Treatment of sample	n_D^{25}
Film from evaporation of latex	1	None	1.5187
	2	do	1.5192
Pale crepe	1	Milled	1.5187
	2	do	1.5188
	3	do	1.5187
Smoked sheet	1	do	1.5188
	2	Milled 5 min	1.5188
	2	Milled 10 min	1.5188
	2	Milled 20 min	1.5189
	2	Milled 30 min	1.5188
Purified	1	(a)	1.5191
	2	(a)	1.5190
	3	(a)	1.5190
	4	(a)	1.5189

[a] See BS J. Research 11; 175 (1933) RP585.

[2] This value is a little higher than the value $n_D^{25}=1.5184$ previously reported by one of the authors, BS J. Research 8, 756 (1932) RP449.

In addition to the studies on plantation rubber, refractive-index measurements were made on twenty samples of representative types of wild rubber, which were kindly furnished by the U. S. Bureau of Plant Industry, Office of Cotton, Rubber, and Other Tropical Plants. The samples ranged in index, n_D^{25}, from 1.5191 to 1.5242, with an average value of 1.5208. The results are not here reported in detail because no study was made to correlate the indices of the various samples with their composition, or to ascertain the indices of the hydrocarbon fractions in the pure state.

All of the above measurements of refractive index relate to the D line of the spectrum. One sample of purified rubber, however, was measured on a Pulfrich refractometer with light of two other wave lengths, and the following results were obtained:

Line	Wave length in angstroms	Refractive index
C (H_α)	6,563	1.5153
D	5,893	1.5190
F (H_β)	4,861	1.5483

The dispersion, $H_\alpha - H_\beta$, was therefore 0.0330.

IV. REFRACTIVE INDEX OF MIXTURES OF UNVULCANIZED RUBBER WITH COMPOUNDING MATERIALS

1. RUBBER-FILLER MIXTURES

Measurements of the refractive index were made on samples of crude rubber mixed with different proportions of whiting, zinc oxide, barytes, titanium dioxide, carbon black, and zinc stearate. Only in the case of zinc oxide was there any significant difference between the index of the mixtures and that of the rubber. A freshly prepared mixture of pale crepe, $n_D^{25}=1.5188$, with 4 percent of "Kadox" zinc oxide showed an index of 1.5220. A mixture of the same rubber with 4 percent of "XX-Red" zinc oxide, however, had an index of 1.5209. With smaller percentages of the two oxides, lower values of the index were obtained. It is probable that some zinc oxide reacted with nonhydrocarbon constituents of the rubber to form salts which dissolved in the rubber and changed the index. A definite statement, however, cannot be made without further experimental work.

As was mentioned previously the addition of filler to rubber increased the difficulty in reading the refractive index by reducing the contrast between the two halves of the field and by rendering the boundary between them less sharp. With carbon black satisfactory observations were obtained for mixtures containing not more than 0.1 percent. With titanium dioxide the amount was of the order of 2 percent. In the case of zinc stearate, however, fairly satisfactory observations were made on stocks containing as high as 50 percent.

2. RUBBER-SULPHUR MIXTURES

When rubber was mixed with sulphur on the mill in proportions up to 4 percent, it was possible to cool the resulting stocks to 25° C and measure the index before any separation of the sulphur or blooming took place. For such stocks the index was a linear function of

the percentage of sulphur, as is indicated by the curve ABC in figure 2. This curve relates to solutions of sulphur in crude rubber and is described by the equation,

$$n_D^{25}=1.5188+0.0016S,$$

where S, is the percentage by weight of dissolved sulphur.

When these stocks were permitted to stand, sulphur separated from those in which it was present in larger amounts, and the index decreased. The measurements after 1 month and 14 months are

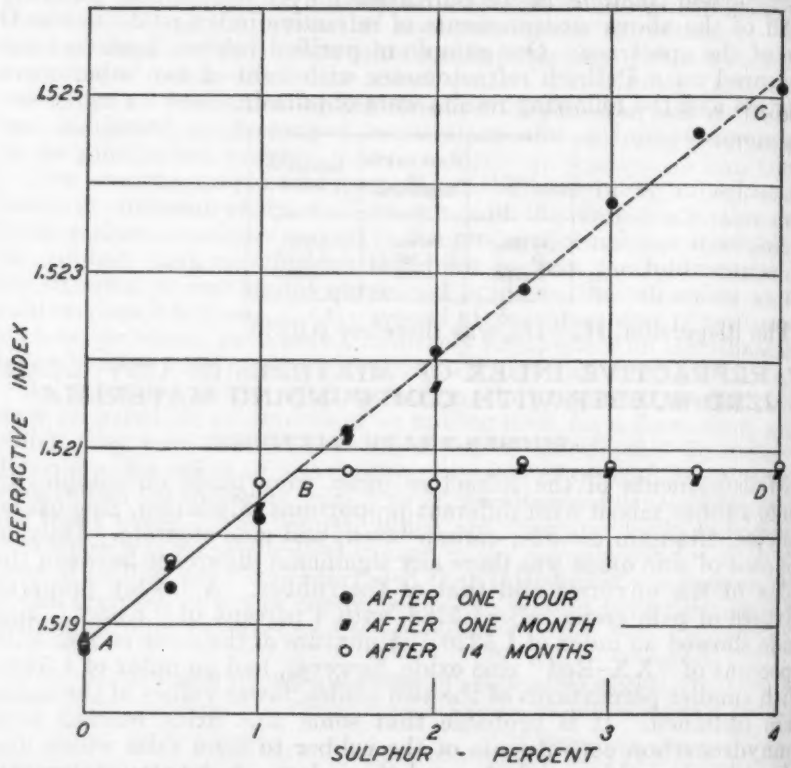

FIGURE 2.—*Refractive index of rubber-sulphur mixtures at different times after mixing.*

AB represents unsaturated solutions of sulphur in rubber; BC, supersaturated solutions; and BD, a saturated solution.

shown in the figure. At the end of 1 month the index of the samples containing from 2.5 to 4.0 percent of sulphur had dropped to the constant value 1.5208, while the index of the samples containing 2.0 percent had dropped a little, and that of the samples containing 1.5 percent was practically unchanged. After 14 months, however, the indices of these last two compositions had dropped to about 1.5208, while those of the other compositions remained practically unchanged. This indicates that the value 1.5208 is the refractive index of a saturated solution of sulphur in rubber at the temperature of the room in which the samples were stored, which was approximately 25° C. As may be seen from the curve, this index corre-

sponds to a solubility of about 1.2 percent. This is somewhat higher than the value 0.85 percent, which is obtained by extrapolation from measurements of the solubility of sulphur in rubber by Morris.[3]

3. MIXTURES OF RUBBER AND PHENYL-β-NAPHTHYLAMINE

Measurements of the refractive index were made on samples which contained from 1 to 8 percent of phenyl-β-naphthylamine and yielded results quite similar to those obtained with the rubber-sulphur stocks. The index of the freshly prepared stocks in which no crystallization had taken place is given by the equation,

$$n_D^{25}=1.5188+0.0015P,$$

where P is the percentage of phenyl-β-naphthylamine. This equation agrees with the observations with a maximum deviation of 0.0003 and an average deviation of 0.0001. When the samples were remeasured after 14 months, those which had contained from 2 to 8 percent of the solute all showed values of n_D^{25}, between 1.5204 and 1.5208, with an average of 1.5206. Taking this as the index of a saturated solution, the solubility of phenyl-β-naphthylamine in rubber is about 1.2 percent. By extrapolation from the measurements by Morris, referred to above, the value 0.7 percent was obtained.

V. REFRACTIVE INDEX OF VULCANIZED RUBBER

Measurements of refractive index were made on vulcanized rubber to determine the relation of the index to the percentage of combined sulphur and the temperature. The samples used were prepared from purified rubber and sulphur in connection with an investigation of the electrical properties.[4] The conditions of vulcanization were such that very nearly all of the sulphur was brought into combination with the rubber. The range of composition on which measurements are here reported extends from 0 to 19 percent of sulphur, or from unvulcanized rubber to semihard rubber. The effect of temperature was investigated for some of the samples, and the range covered was from about 10 to 75° C.

1. EFFECT OF COMBINED SULPHUR AT 25° C

The refractive indices of rubber-sulphur compounds are presented graphically in figure 3, in which the index is plotted against the percentage of combined sulphur. The index bears a linear relation to the sulphur content up to 16 percent. The only higher point shown is at 19 percent of sulphur and falls below the line for a reason which will be discussed in the next section of this paper. Few of the measurements were made at exactly 25° C. In some instances the refractive indices at 25° C were read from a curve which related the indices to temperature. Most of the measurements, however, were made at temperatures which differed from 25° by only 1 or 2° C, and were reduced to this standard temperature by the use of the temperature coefficient discussed in a later paragraph. The relation shown in

[3] Ind. Eng. Chem. 24, 584 (1932).
[4] Scott, McPherson, and Curtis, BS J.Research 11, 173 (1933) RP585.

figure 3 between the refractive index at 25° C and the percentage of sulphur is described by the equation,

$$n_D^{25}=1.5190+0.00370\ S_c$$

where S_c is the combined sulphur expressed in percentage. In a report [5] describing preliminary measurements the index was expressed as a linear function of the sulphur content in terms of atoms of sulphur per C_5H_8, but the present results indicate a more nearly linear relation when the sulphur is given in percentage by weight.

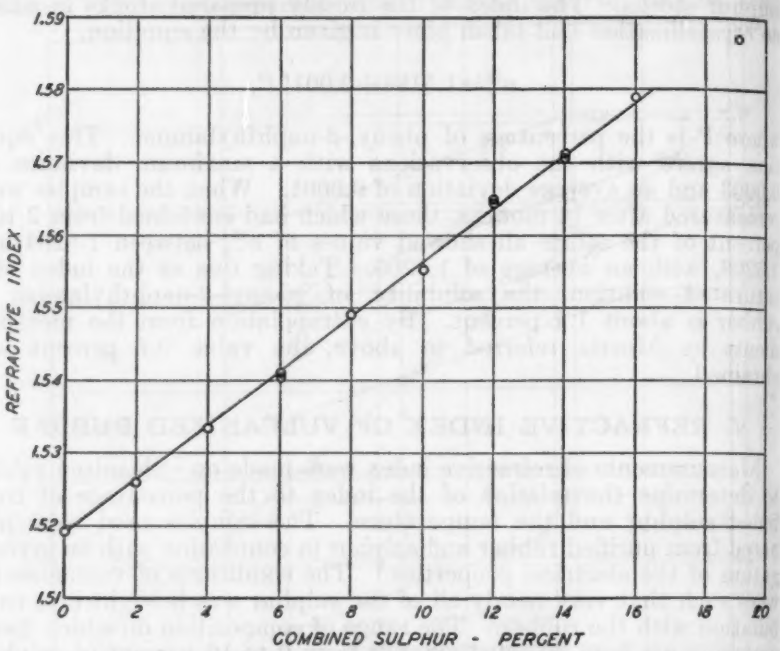

FIGURE 3.—*Relation of refractive index of rubber-sulphur compounds at 25° C to percentage of combined sulphur*

2. EFFECT OF TEMPERATURE

Measurements of the refractive index of rubber-sulphur compounds are also presented graphically in figure 4, in which they are plotted against the temperature. In the range of temperature under consideration the index of the samples containing from 0 to 16 percent of sulphur decreased linearly with increasing temperature. The change in index per degree centigrade was from 0.000345 to 0.00036, with an average value of 0.00035. This is in reasonable agreement with the change in index, 0.00036 per degree centigrade, reported in a previous investigation by one of the authors.[6] Kirchhof[7] has measured the refractive indices of a number of samples of crude rubber at different temperatures. His observations indicate a change in index of from 0.00034 to 0.00042 per degree centigrade, with an average of 0.00039.

[5] BS Tech. News Bul. 194, p. 66 (June 1933).
[6] A. T. McPherson, BS J. Research 8, 751 (1932) RP449.
[7] Kautschuk 8, 137 (1932); also Rubber Chem. Tech. 6, 92 (1933).

When the relation between refractive index and temperature is combined with the relation between refractive index and sulphur content, the following expression is obtained,

$$n_D^t = 1.5190 + 0.0037OS_c - 0.00035\ (t-25)$$

where S_c is the percentage of combined sulphur, and t, the temperature in degrees centigrade. The maximum deviation of observations at different temperatures from values computed by this equation was 0.0015 and the average deviation was 0.0006.

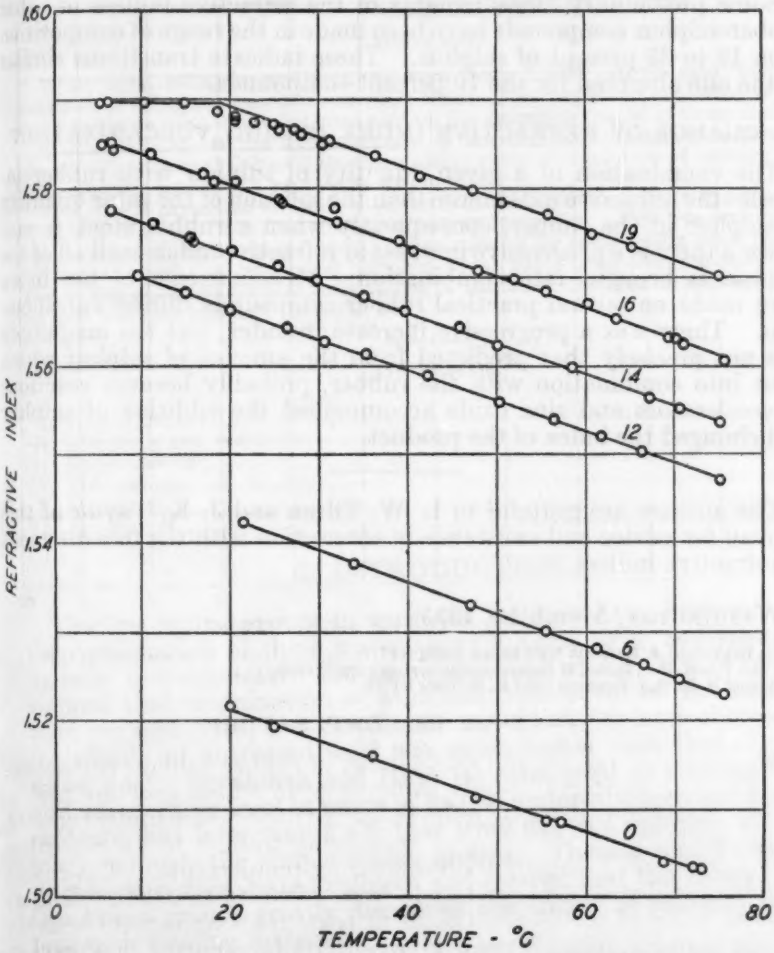

FIGURE 4.—*Relation of refractive index of rubber-sulphur compounds to temperature.*

The figures on the different curves denote the percentages of combined sulphur.

The curve in figure 4, which relates the refractive index of the compound containing 19 percent of sulphur to the temperature, shows a change in slope at approximately 17° C. This point represents the intersection of two straight lines drawn through the points above and below the transition, respectively. As indicated by the observations,

however, the transition is not sharp but gradual, and this is probably the reason why the index at 25° C does not fall quite in line with the indices of compounds containing lower percentages of sulphur. The transition is probably of the type designated by Ehrenfest as a transition of the second order.[8] Such a transition is indicated in the same region of temperature for a compound containing 19 percent of sulphur, by temperature-volume measurements. The temperature-volume measurements by Kimura and Namikawa[9] indicate a transition at about 30° C, and those by Scott,[10] at about 34° C.

Some preliminary measurements of the refractive indices of other rubber-sulphur compounds have been made in the range of composition from 19 to 32 percent of sulphur. These indicate transitions similar to the one observed for the 19 percent compounds.

3. CHANGE OF REFRACTIVE INDEX DURING VULCANIZATION

The combination of a given quantity of sulphur with rubber increases the refractive index more than the solution of the same quantity of sulphur in the rubber, consequently when a rubber stock is vulcanized there is a progressive increase in refractive index until all of the sulphur is brought into combination. Measurements of the index were made on several practical rubber compounds during vulcanization. There was a progressive increase in index, but the magnitude was not precisely that predicted from the amount of sulphur which went into combination with the rubber, probably because reactions of accelerators and zinc oxide accompanied the addition of sulphur and changed the index of the product.

The authors are grateful to L. W. Tilton and J. K. Taylor of this Bureau for advice and assistance in connection with the measurement of refractive indices.

WASHINGTON, March 11, 1935.

[8] See Bekkedahl, J. Research NBS **13**, 424 (1934) RP717.
[9] J. Soc. Chem. Ind., Japan, **32** (supplemental binding), 196B (1929).
[10] Arnold H. Scott, J. Research NBS **14**, 99 (1935) RP760.

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AMINO-NITROGEN CONTENTS OF WOOL AND COLLAGEN

By Joseph R. Kanagy[1] and Milton Harris[2]

ABSTRACT

When wool, collagen, and arginine were treated with nitrous acid, increasing amounts of nitrogen were evolved with time. The continued evolution of nitrogen was due to the action of nitrous acid on the guanidine nuclei of these materials.

A new method for the determination of the arginine content of a protein is given. The method is based on the relative rates of evolution of nitrogen from the guanidine nuclei in a protein and in arginine.

Evidence is presented to show that the action of nitrous acid on the guanidine nucleus is different from its action on a free amino group. The free amino-nitrogen contents of wool and collagen were calculated by subtracting from the total nitrogen evolved that portion of nitrogen which came from the guanidine nuclei. The values obtained for the percentages of the total nitrogen as amino nitrogen are 2.53 for wool and 2.77 for collagen.

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I. INTRODUCTION

The free amino groups in wool and collagen have been related to the combination of these materials with acids, dyes, and tannins by various investigators. Trotman (1),[3] and Benz and Farrel (2) claimed that deamination of wool had little effect on the affinity of wool for acid dyes, but Speakman and Stott (3) later showed that the affinity of untreated wool was much higher than that of deaminated wool. Speakman and Hirst (4) attempted to account for the acid adsorbed by wool in terms of its free amino nitrogen and histidine contents, but later stated (3) that wool did not combine with acid solely through the simple amino groups. Thomas and Foster (27) worked with deaminated collagen and showed that the absence of the free amino groups greatly decreased the ability of collagen to combine with tanning material.

The method employed by all of these investigators for the determination of the free amino groups is based on the reaction between these groups and nitrous acid, whereby the nitrogen of the amino

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[3] Figures in parentheses here and throughout the text refer to the references given at the end of this paper.

group is liberated and the amino group is replaced by a hydroxyl group according to the following scheme:

$$R-\underset{\underset{COOH}{|}}{CH}-NH_2+HNO_2 \rightarrow R-\underset{\underset{COOH}{|}}{CH}-OH+H_2O+N_2 \qquad [1]$$

The values they obtained for the amino-nitrogen contents varied greatly. The results of the present investigation show that their values do not necessarily represent the true amino-nitrogen content, and were dependent on the conditions under which their determinations were made. Owing to these discrepancies their attempts to relate the free amino nitrogen to chemical combination were solely of a qualitative nature.

II. MATERIALS AND METHODS

A number of methods are now available for the determination of amino nitrogen. The advantages and limitations of each have been compared and discussed by a large number of workers (5) (6). While none of the methods is entirely satisfactory for the determination of amino nitrogen in complex mixtures, the method of Van Slyke, which is based on the reaction in equation 1 appears to be the best for estimating the free amino nitrogen in native proteins.

In this work a Van Slyke macro-apparatus (7) was used. Since the amounts of amino nitrogen obtained were small, a 3-ml gas burette was substituted for the standard 40-ml burette. The nitrous acid was obtained by the interaction of equivalent quantities of sodium-nitrite and acetic acid. The apparatus was calibrated to deliver 9.72 ml of glacial acetic acid and 38.88 ml of a 30-percent solution of sodium nitrite to the reaction vessel. After the air in the reaction vessel was displaced by nitric oxide, formed by the decomposition of the nitrous acid, all but 5 ml of the nitrous acid was forced out of the reaction vessel. The reaction vessel is calibrated to hold 20 ml of nitrous acid. However, it was found advantageous to dilute the nitrous-acid solution. The dilute solution evolved much less nitric oxide, gave more reproducible blanks, and caused less frothing. The nitrous acid remaining in the vessel was diluted with 10 ml of water, and then 10 ml of the solution to be analyzed was introduced.

At different intervals of time, the gas evolved was run into a Hempel pipette containing an alkaline permanganate solution, which absorbed the nitric oxide. The volume of nitrogen was measured and the temperature and pressure were noted. The weight of a given volume of nitrogen at a known temperature and pressure was read directly from a table prepared by Van Slyke (7). The values obtained were corrected for the amount of nitrogen obtained in blank determinations, which were made for each time interval.

The experimental errors were minimized by keeping the stopcocks well greased, changing the permanganate solutions after every five or six runs, using freshly prepared and more dilute solutions of nitrous acid, and making blank determinations under the identical conditions of the original determinations.

One of the sources of error in amino-nitrogen determinations by the Van Slyke method occurs in making a correction for the amount of nitrogen evolved by the spontaneous decomposition of the nitrous

acid itself. Since the amount of free amino nitrogen present in native proteins is very small, it is obvious that much care must be exercised in making such corrections. For a given time of reaction, the size of the blank depends on the age of the sodium-nitrite solution, and the rate of evolution of the gas. The latter, in turn, depends on the speed of shaking and on the nature of the material being analyzed. For example, suspended particles cause a more rapid evolution of gas than materials in true solution. The effects of the various factors are illustrated in table 1. The blank determinations were made both

TABLE 1.—*Effect of various factors on the volume of nitrogen obtained in blank determinations*

Blank	Time of reaction	Age of $NaNO_2$ solution	Volume of gas [1] evolved	Volume of nitrogen
			ml	ml
Water	5 min	1 hr	75	.37
Do	5 min	24 hr	75	.43
Do	5 min	3 days	75	.48
Do	5 min	7 days	75	.49
Do	5 min	7 days	125	.55
Cellulose	5 min	1 hr	75	.43
Water	15 min	1 hr	85	.42
Cellulose	15 min	1 hr	85	.46
Water	30 min	1 hr	100	.43
Cellulose	30 min	1 hr	100	.48
Water	2 hr	1 hr	125	.51
Cellulose	2 hr	1 hr	125	.53
Water	20 hr	1 hr	150	.91
Cellulose	20 hr	1 hr	150	.90

[1] The volume of gas evolved was estimated and the values are accurate to about ± 5 ml.

on 10-ml portions of distilled water and on 10-ml portions of a 1-percent suspension of powdered cellulose. The initial amounts of nitrogen evolved were higher when powdered cellulose was used than with water alone, but they became about equal after 2 hours. In the subsequent determinations on the wool and collagen suspensions, the corrections applied were obtained on blanks containing about the same weights of cellulose as of the protein used. In all determinations the reaction vessel was shaken during the last 3 minutes.

The wool used was prepared from raw stock which had been extracted with alcohol and ether and washed with water. The clean fibers were ground in a pebble mill for 48 hours and the total nitrogen of the resulting powder was determined. The values were corrected for ash and moisture.

Standard hide powder, American Leather Chemists Association 1933, prepared in the same manner as the wool, was used for the determinations on collagen.

The suspensions were prepared by shaking approximately 1-g samples of the powder (particle size 0.3 to 2.0μ) in 100 ml of water. A 10-ml aliquot of the suspension was measured in the graduated cylinder of the Van Slyke apparatus and run into a Kjehldahl flask for determination of total nitrogen. Another 10-ml aliquot was then measured in the same cylinder and run into the Van Slyke apparatus for determination of amino nitrogen.

The glycine and arginine hydrochloride were from the Eastman Kodak Co.

III. EXPERIMENTAL

While it is known that the α-amino groups of the individual amino acids react completely with nitrous acid in 5 to 10 minutes, the time required for the amino nitrogen in proteins may be much longer. As a preliminary investigation, the evolution of amino nitrogen from glycine when treated with nitrous acid for different lengths of time was determined. The rates of evolution of nitrogen from the nitrous acid alone and from the nitrous acid plus the glycine are shown in figure 1. Since the curves are parallel, it is obvious that the increasing amounts of nitrogen, obtained by prolonging the time of reaction, come from the nitrous acid itself. The amino-nitrogen content of glycine at any time is obtained by subtracting the values on the lower curve from the corresponding values on the upper curve. These results are given in table 2. The high values obtained are in accord with those found by Van Slyke (8), and Levene and Van Slyke (9),

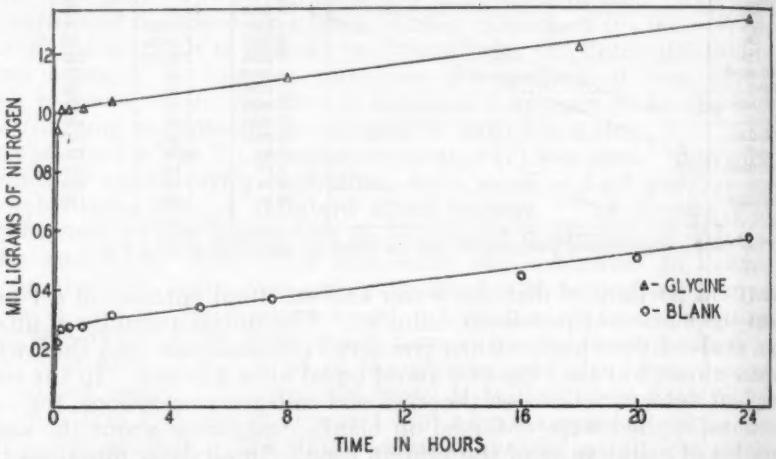


FIGURE 1.—*Relative rates of evolution of nitrogen from nitrous acid alone and from nitrous acid and glycine.*

who obtained values of 103 to 107 percent of the total nitrogen of glycine as amino nitrogen. The anomalous results appear to be independent of time and to depend on some specific reaction of the glycine or its reaction product with nitrous acid. Van Slyke's analyses of alanine gave values of 99.3 to 100.5 percent of the total nitrogen as amino nitrogen.

TABLE 2.—*Amino-nitrogen content of glycine*

Time	Total nitrogen as amino nitrogen
	Percent
5 min	99.2
15 min	105.5
30 min	103.6
1 hr	103.2
2 hr	102.5
8 hr	106.3
18 hr	105.6
24 hr	105.7

When 1-percent suspensions of powdered wool and collagen were treated with nitrous acid for different lengths of time and the necessary corrections for blank determinations applied, the values obtained were not constant as in the case of the mono-amino acids, but increased with increase in time of reaction. The results are shown in figure 2. In the case of wool, this increase in the amount of nitrogen evolved with time had been previously noted by Meunier and Rey (10), and by Speakman and Hirst (4).

Since the pH of the nitrous-acid solutions was about 4, there was little reason to believe that the increased evolution of nitrogen was due to a hydrolysis occurring during the reaction. The absence of hydrolysis was demonstrated by treating wool and collagen for periods

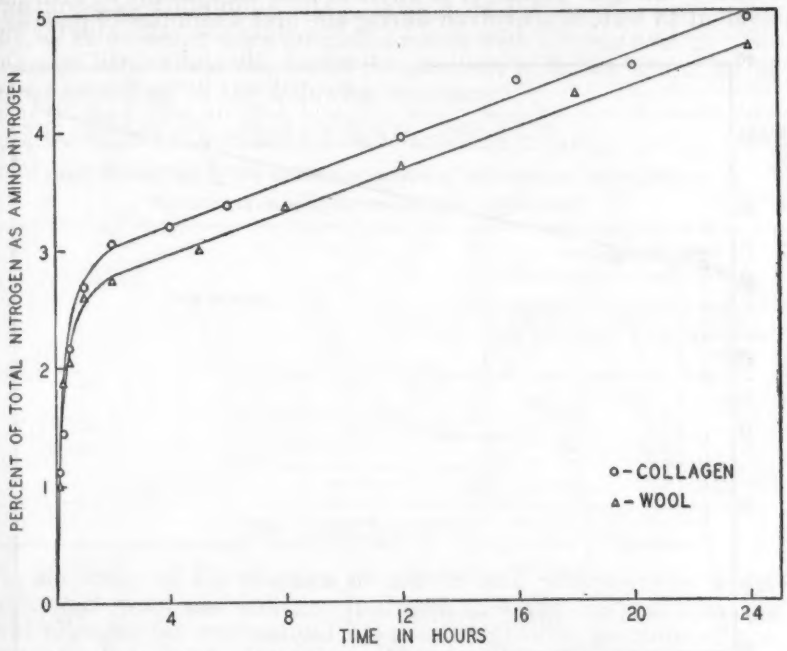


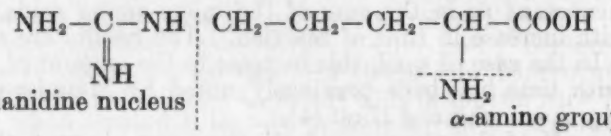
FIGURE 2.—*Rate of evolution of nitrogen from wool and collagen.*

of 24 and 48 hours with sodium-acetate-acetic-acid solutions containing acid and salt in amounts approximately equivalent to, and at about the same pH as those found in the nitrous-acid solutions. The specimens thus treated showed no measurable increase in amino-nitrogen content by the Van Slyke method.

In the absence of any hydrolysis it seemed probable that the increasing amounts of nitrogen obtained might be formed by the slow interaction of nitrous acid with a nitrogen-containing group other than an amino group.

Although the Van Slyke method has been shown to give high amino-nitrogen values for a number of the individual amino acids (8) (9), the only amino acid present in wool and collagen in appreciable amounts, which is known to give off increasing amounts of nitrogen

with time is arginine (11). Its structural formula is represented as follows:



It seemed logical, therefore, to study the rate of evolution of nitrogen from this amino acid under conditions identical with those used for wool and collagen. The results are shown in figure 3. Since arginine contains 4 nitrogen atoms, it is obvious that an amount of nitrogen equivalent to 1 atom is evolved during the first 5 minutes of reaction.

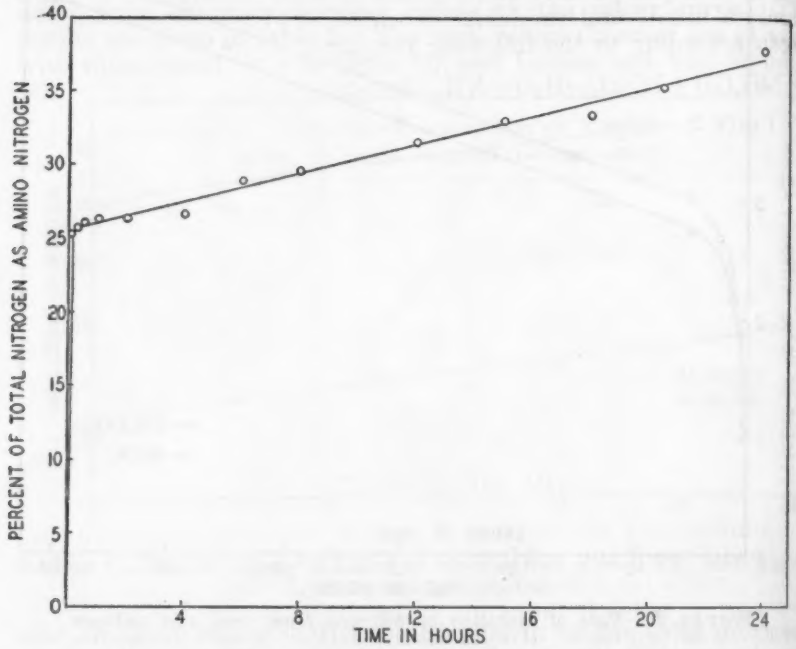


FIGURE 3.—*Rate of evolution of nitrogen from arginine.*

This nitrogen comes from the α-amino group. The nitrogen subsequently evolved is formed by the action of nitrous acid on the guanidine nucleus.

The exact structure of guanidine or the guanidine nucleus is not known, but most investigators agree that the NH_2 group, if one is present, is not a true free amino group. Their evidence will be presented later. That the nitrogen evolved by the interaction of nitrous acid with the guanidine nucleus was not produced in the same manner as nitrogen obtained by the action of nitrous acid on a free amino group was further demonstrated by the following experiments. Tenth-gram portions of arginine hydrochloride were introduced into Kjehldahl flasks and 25 ml of a nitrous-acid solution of the same concentration as used previously in the Van Slyke analyses was added to

each. After the reaction had proceeded for a definite interval of time, the solution was diluted to about 200 ml, an excess of magnesium oxide added, and the amount of ammonia in the solution was distilled off and determined. For controls, 0.1-g portions of arginine hydrochloride were treated with acetic acid and 0.1-g portions of glycine were treated with nitrous acid in the same manner. The results are recorded in table 3. The reactions of nitrous acid with the guanidine nucleus are complicated, and it is not desired to place any emphasis on these results as a possible explanation of the mechanism of the reactions. However, the data show that ammonia is a product of at least one of the reactions, and that the amount of ammonia present in the solutions reaches a maximum and then decreases with time. This is to be expected since ammonia reacts with nitrous acid to form ammonium nitrite and the latter decomposes with the liberation of nitrogen according to the following reactions:

$$NH_4OH+HNO_2 \rightarrow H_2O+NH_4NO_2 \rightarrow 2H_2O+N_2\uparrow \quad [2]$$

TABLE 3.—*Effect of the continued action of nitrous acid on arginine*

[Values given are in milligrams per gram of amino acid]

Time in hours	Ammonia nitrogen		
	Glycine treated with HNO_2	Arginine treated with HNO_2	Arginine treated with acetic acid
	mg	mg	mg
3	0.5	21.4	0.7
6	.6	25.1	.6
24	.8	20.3	.8
48	.9	12.3	1.2
72	----------	6.6	1.3

IV. DISCUSSION

The similarity of the reaction of nitrous acid with arginine to its reaction with wool and collagen indicates that the continued evolution of nitrogen (as represented by the straight-line portions of the curves in fig. 2) is due to the action of the nitrous acid on the guanidine nuclei of these proteins. If it is assumed that all of this portion of the total nitrogen evolved comes from the guanidine nucleus, then the fraction of the total nitrogen of the protein as arginine nitrogen is equal to the ratio of the slope of the curves for wool or collagen (fig. 2) to the slope of the curve for arginine (fig. 3). It is thus possible to calculate the arginine contents of these materials from the following equations:

$$A=\frac{(F_A)(N_P)}{(N_A)}\times 100 \quad [3]$$

where:

A = the arginine content of the protein in percent
F_A = the fraction of the total nitrogen of the protein as arginine nitrogen
N_P = the nitrogen content of the protein
N_A = the nitrogen content of arginine

$$F_A=S_P/S_A \quad [4]$$

where:

S_P=the slope of the straight line portion of the curve for proteins

S_A=the slope of the straight line portions of the curve for arginine.

Substituting equation 3 in 4

$$A=\frac{(S_P)(N_P)}{(S_A)(N_A)}\times 100 \qquad [5]$$

The slope of the curve for collagen is 0.0875, for wool 0.0865, and for arginine 0.488. The corresponding nitrogen contents are 17.40, 16.32, and 32.18 percent. Substituting these figures in equation 5, the arginine contents of the wool and collagen were found to be 9.0 and 9.7 percent, respectively.

By methods of isolation, Stewart and Rimington (12), and Vickery and Block (13) found 6.0 and 7.8 percent, respectively, of arginine in wool. Marston (14), employing indirect methods, found 10.2 percent. The arginine content of collagen has been reported as 8.2 percent by Dakin (15), and as 7.62 by Fischer, Levene, and Aders (16). These values were also obtained by isolation of the amino acid. The separation of amino acids by isolation from protein hydrolysates is a long and tedious process, and, at best, cannot be carried out without the loss of a considerable portion of the material. The summation of the amino acids of most of the proteins analyzed accounts for only about 65 to 85 percent of the protein. In view of the fact that isolation methods for amino acids are known to give low results, the method described in this paper may be considered to give better values for the arginine contents of wool and collagen.

The amino-nitrogen contents of wool and collagen were obtained by subtracting from the total nitrogen evolved that portion of the nitrogen evolved from the guanidine nucleus of the arginine in these materials. The arginine contents were those calculated in this paper. The calculations were made with the experimental values and are not points taken from the smooth curves. The results are recorded in table 4. From the average values in table 4 and the nitrogen contents of wool and collagen, the percentages of the total nitrogen as amino nitrogen were found to be 2.53 and 2.77, respectively.

TABLE 4.—*Amino nitrogen contents of wool and collagen*

[Values given are in milligrams per gram of protein]

WOOL

Time in hours	Total nitrogen evolved	Arginine nitrogen	Amino nitrogen
	mg	mg	mg
2	4.48	0.38	4.10
5	4.89	0.85	4.04
8	5.46	1.30	4.16
12	5.96	1.88	4.08
18	6.96	2.52	4.44
24	7.66	3.68	3.98
Average			4.13

TABLE 4.—*Amino nitrogen contents of wool and collogen*—Continued

COLLAGEN

Time in hours	Total nitrogen evolved	Arginine nitrogen	Amino nitrogen
	mg	mg	mg
2	5.30	0.41	4.89
4	5.56	0.53	5.03
6	5.83	1.25	4.58
12	6.88	2.03	4.85
16	7.66	2.66	5.00
20	7.92	3.22	4.70
24	8.62	3.97	4.65
Average			4.82

It is apparent from the above calculations that in this work the free amino groups have been considered to be only those that react with nitrous acid according to equation 1. Bracewell (17) suggested that other free amino groups are present in the protein molecule, but they are anomalous in that they do not react with nitrous acid. The investigations of Werner (18) showed, however, that anomalous amino groups have no real existence. Bancroft and Ridgway (19) summarized the work on the reactions of nitrous acid and guanidine. They found that various formulas have been assigned to the latter to account for its behavior, but that the experimental data did not conclusively favor any one formula. From their own investigations they concluded that guanidine and pure nitrous acid did not react, that excess acid other than nitrous acid catalyzed the reaction [4], and that the rate of evolution of nitrogen depended on the concentration of nitrous acid, the hydrogen-ion concentration, and a specific effect due to the acid itself. Clark and Gillespie (20) showed that in the presence of sodium carbonate, benzenesulphonyl chloride combined only with the α-amino group in arginine. The evidence indicates that an amino group does not exist in guanidine, or, if one does exist, it does not function as a free amino group.

Whether or not the guanidine nucleus is considered to contain a free amino group, it is obvious that treating a native protein with nitrous acid for an arbitrary length of time will not necessarily give a value which represents the true amino-nitrogen content of that protein. Meunier and Rey (10), on treating wool with nitrous acid for 7 hours, found that 5.7 mg of nitrogen was evolved from each gram of material. They assumed this to be the content of free amino nitrogen. Speakman and Hirst (4) likewise treated wool for 24 hours and obtained values of 9.2 and 11.9 mg of nitrogen per gram of wool. Subsequently, Speakman and Stott (3) studied the action of three concentrations of nitrous acid on wool and stated: "It is evident that the amino-nitrogen content of wool cannot be defined with any degree of precision. The rate of evolution of nitrogen depends to a striking extent on the concentration of nitrous acid * * *." They also determined the acid-combining capacity of untreated and deaminated wool, and found that the latter retained slightly more than half of its maximum combining capacity for

[4] Acetic acid is always present in the Van Slyke procedure. It is apparent, therefore, that the slopes of the curves will depend on the conditions under which the reactions are run.

hydrochloric acid. They concluded that the nitrogen liberated from wool could scarcely be derived solely from the arginine and lysine side-chains, and in view of a recent study of the action of nitrous acid on cystine (24) it seemed likely that part of the nitrogen was derived from the action of nitrous acid on the sulphur linkage. Lough and Lewis (24), in their studies of the action of nitrous acid on cystine, found that "extra" nitrogen was obtained only when oxidation of sulphur to sulphate occurred. Recently an attempt (25) was made in this laboratory to oxidize the sulphur in wool to sulphate with bromine and hydrochloric acid. Even with such a strong oxidizing agent only very small amounts of sulphate were obtained in periods of 24 and 48 hours. In view of this and the fact that the sulphur in wool has very different properties in general from the sulphur in cystine, it hardly seems justifiable to assume the formation of "extra" nitrogen.

The similarity of the behavior of the guanidine nucleus of the arginine in wool and collagen with that of the guanidine nucleus of the arginine itself indicates that the former is free in the native protein. Since the guanidine group is a strong base and readily combines with acids, it should be possible to account for the acid taken up by wool and collagen by their free amino groups and guanidine nuclei. Bancroft and Ridgway (19) stated that guanidine is a mono-acid base, while Schmidt, Kirk, and Appleman (21) determined the titration curve of arginine and found that arginine monohydrochloride combines with one equivalent of hydrochloric acid. On the basis of the amino groups and guanidine nuclei each combining with one equivalent of acid, the amounts of acid that will combine with wool and collagen have been calculated. The results are given in table 5. The calculated values are in good agreement with those obtained experimentally.

TABLE 5.—*Amounts of acid combined with wool and collagen*

[Values given are in milliequivalents of acid per gram of protein]

Material	Calculated	Experimental
	Milliequivalents	*Milliequivalents*
Wool	0.81	0.80 (4)
Collagen	.90	1.0 (22) .899 (23) .98 (26)

The observations of Hitchcock (23), and of Speakman and Stott (3) that deaminated gelatin and wool retain a considerable portion of their acid-combining capacities are of interest, especially since the deaminated materials were prepared under very different conditions. Gelatin was treated for 30 minutes with nitrous acid, and 5.6 mg of nitrogen, which was equivalent to slightly more than its free amino nitrogen, was removed. Wool was treated for 72 hours and about 9 mg of nitrogen was removed. This accounts for the free amino nitrogen and nearly one atom of nitrogen from the guanidine nucleus. The acid-combining capacities of the deaminated proteins are given in table 6. The results indicate that the removal of a nitrogen atom from the guanidine nucleus has not appreciably altered the latter's

basic properties. The evidence suggests the possibility that the nitrogen atom, which is most readily removed by treatment with nitrous acid, is not the nitrogen which combines with the acid.

TABLE 6.—*Acid-combining capacities of deaminated gelatin and wool*

Material	Acid combined, per gram	Calculated acid-combining capacity of the guanidine nuclei
	Milliequivalents	*Milliequivalents*
Gelatin (23)	0.44	0.56
Wool (3)	.43	.52

V. CONCLUSION

The results of the investigation show that when wool, collagen, and arginine are treated with nitrous acid, increasing amounts of nitrogen are evolved with time. The continued evolution of nitrogen is due to the action of nitrous acid on the guanidine nuclei of these materials. Since the evidence indicates that the nitrogen which comes from the guanidine group is not free amino nitrogen, the amino-nitrogen contents of wool and collagen are calculated by correcting for the guanidine nitrogen evolved. The values obtained for the percentages of the total nitrogen as amino nitrogen are 2.53 for wool and 2.77 for collagen.

VI. REFERENCES

(1) E. R. Trotman, The relation between the nitrogen of wool and its affinity for acid and basic dyes. J. Soc. Dyers Colourists **40,** 77 (1924).
(2) E. Bentz and F. J. Farrel, A note on the theory of dyeing. J. Soc. Chem. Ind. **16,** 405 (1897).
(3) J. B. Speakman and E. Stott, A contribution to the chemical theory of dyeing: The affinity of deaminated wool for acid dyes. J. Soc. Dyers Colourists **50,** 341 (1934).
(4) J. B. Speakman and M. C. Hirst, The constitution of the keratin molecule. Trans. Faraday Soc. **29,** 148 (1933).
(5) H. H. Mitchell and T. S. Hamilton, The Biochemistry of the Amino Acids, pp. 94–140 (Chemical Catalog Co., New York, 1929).
(6) G. M. Richardson, Critique on the biological estimation of amino nitrogen. Proc. Royal Soc. [B] **115,** 142 (1934).
(7) D. D. Van Slyke, The quantitative determination of aliphatic amino groups. J. Biol. Chem. **12,** 277 (1912).
(8) D. D. Van Slyke, Determination of amino groups. J. Biol. Chem. **9,** 185 (1911).
(9) P. A. Levene and D. D. Van Slyke, The composition and properties of glycocoll picrate and the separation of glycocoll from alanine. J. Biol. Chem. **12,** 285 (1912).
(10) L. Meunier and G. Rey, Sur les propriétés de la laine. J. Int. Soc. Leather Trade Chem. **11,** 509 (1927).
(11) R. H. Plimmer, The action of nitrous acid on hezone bases. Biochem. J. **18,** 105 (1924).
(12) A. M. Stewart and C. Rimington, Basic amino acids of wool. Biochem. J. **25,** 2189 (1931).
(13) H. B. Vickery and R. J. Block, Basic amino acids of wool. J. Biol. Chem. **86,** 107 (1930).
(14) H. R. Marston, The chemical composition of wool. Bull. 38, Commonwealth of Australia Council for Scientific and Industrial Research (1928).
(15) H. D. Dakin, Amino acids of gelatin. J. Biol. Chem. **44,** 499 (1920).

(16) E. Fischer, P. A. Levene, and H. P. Aders, Über die Hydrolyse des Leims. Z. Physiol. Chem. **35,** 70 (1902).
(17) R. S. Bracewell, The molecular mechanism of colloidal behavior. J. Am. Chem. Soc. **41,** 1511 (1919).
(18) E. A. Werner, The Chemistry of Urea. (London, 1923.)
(19) W. D. Bancroft and S. L. Ridgway, Guanidine and nitrous acid. J. Phys. Chem. **35,** 2950 (1931).
(20) H. T. Clark and H. B. Gillespie, Benzensulfonylguanidine. J. Am. Chem. Soc. **54,** 1964 (1932).
(21) C. L. A. Schmidt, P. L. Kirk, and W. K. Appleman, The apparent dissociation constants of arginine and of lysine and the apparent heats of ionization of certain amino acids. J. Biol. Chem. **88,** 285 (1930).
(22) D. Jordan Lloyd and C. Mayes, Titration curve of gelatin. Proc. Roy. Soc. [B] **93,** 69 (1922).
(23) D. T. Hitchcock, The combination of deaminized gelatin with hydrochloric acid. J. Gen. Physiol. **6,** 94 (1923–24).
(24) S. A. Lough and H. B. Lewis, The reaction of nitrous acid with cystine and related sulphur-containing compounds. J. Biol. Chem. **104,** 601 (1934).
(25) Unpublished report. M. Harris.
(26) John Beek Jr., The combining weight of collagen. J. Research NBS **14** 217 (1935) RP765.
(27) A. W. Thomas and S. B. Foster, The behavior of deaminized collagen. J. Am. Chem. Soc. **48,** 489 (1926).

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FIRE-RESISTANT DOPED FABRIC FOR AIRCRAFT

By Gordon M. Kline

ABSTRACT

Cellulose nitrate dope now commonly used to cover the fabric on the wings and fuselage of airplanes is very flammable and its replacement by a less-hazardous product is desirable. The development of a satisfactory nonflammable dope by the use of natural and synthetic resins or mixtures of synthetic resins with cellulose nitrate and cellulose acetate has not proved to be feasible. An airplane covering with very good resistance to ignition may be obtained by the application of a 3:7 boric-acid-borax mixture to airplane cloth and subsequently doping it with cellulose acetate. Cellulose acetate dope is now only moderately more expensive than cellulose nitrate dope. The cost difference becomes insignificant when the lower fire hazard resulting from the use of the much less flammable cellulose acetate dope is considered.

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I. INTRODUCTION

The rapid growth of the aviation industry in this country has brought to the fore the problem of eliminating the fire hazard inherent in fabric doped with cellulose nitrate, now commonly used to cover the wings and fuselage of airplanes. The destruction of costly aircraft because of the accidental ignition of the flammable covering by the backfiring of the motor, the careless toss of a lighted match or cigarette, or the chance settling of a spark from a nearby flue, has become too general an occurrence. The rapid spread of flames following a minor crash presents a formidable obstacle to the rescue of trapped survivors. It has been stated that the use of metal will eliminate this hazard, but

it is probable that, particularly for service airplanes, fabric will continue in use for some time to come because of its lower cost, availability, and ease of application, factors which facilitate rapid replacement of losses in time of war. An investigation was, therefore, undertaken by the National Bureau of Standards, with the financial assistance of the National Advisory Committee for Aeronautics, to develop a nonflammable doped fabric for aircraft.

The use of cellulose nitrate and cellulose acetate in airplane dopes during the war has been described by Esselen (3),[1] Smith (5) Deschiens (10, 11, 12, 17, 23, 25), Drinker (18), and Britton (28, 29). Very little work on the use of other materials for airplane dopes has been reported. Two Japanese investigators, Araki and Nagamote, have described experiments with ethylcellulose (37) and benzylcellulose (43). Deschiens (23) foresaw the day when "the formates, butyrates, oxalates, and benzoates of cellulose, the phenylcelluloses, the esters of the higher fatty acids, and many other cellulose derivatives that are now being explored will be of industrial importance." Gardner (39) recommended a study of phthalic anhydride-glycerin resins for coating wing surfaces. Other resins and cellulose esters and ethers have been proposed for airplane dopes in various patents, but no detailed study of the properties of these compounds relating to their satisfactory use for such purpose has been published. This paper presents the results of a comparative study of cellulose nitrate, cellulose acetate, and various natural and synthetic resins as constituents of airplane dopes, with particular emphasis upon the development of a nonflammable doped fabric. The effect of fireproofing airplane cloth on the fire resistance of the product covered with cellulosic dopes has also been determined.

A satisfactory airplane dope should tauten the fabric to which it is applied, dry relatively rapidly without "blushing", i. e., precipitating the cellulose derivative in white patches because of moisture condensation, give a smooth, durable surface, and permit a low film weight. To these we believe should be added the requirement that the doped fabric should be fire resistant. The properties of the doped fabric which were measured in this study were weight, tautness, and flammability. Resistance to weathering, which necessarily requires long periods for its determination, was not investigated in this exploratory work, but was reserved for later study with those materials which satisfy the other requirements.

II. TEST METHODS

1. TAUTNESS OF DOPED FABRIC

Square panels 12 inches (30.5 cm) inside dimension were prepared from 1.5 by 0.75 inch (3.8 by 1.9 cm) dressed white pine.[2] Grade A mercerized cotton airplane cloth, corresponding to U. S. Navy Department specification 27c12, was applied to one face only of the panel and fastened by tacks along the sides at intervals of about 1.5 inches (3.8 cm). The various materials, dissolved in suitable solvents, were brushed on the cloth, usually by a four-coat application. After drying overnight at room temperature, the panels were placed in a

[1] The numbers in parentheses refer to the bibliography at the end of this paper.

[2] In later work not reported in this paper square panels 12.25 inches (31.1 cm) inside dimension prepared from 1.5 by 1 inch (3.8 by 2.5 cm) spruce strips according to U. S. Naval Aircraft Factory proposed aeronautical process specification for covering of panels for exposure tests, SP–16, dated October 6, 1932, were used and are considered to be preferable.

room kept at about 21° C and 65 percent relative humidity. After approximately 48 hours the tautness was determined with a McGowan tautness meter (47) (see fig. 1). The values given in the tables for the tautness determinations are the deflections of the plunger, resting on the doped surface, when a load of 15 ounces (425 grams) is added. It is considered that for satisfactory tautness the deflection caused by the 15-ounce weight should not be greater than 0.130 inch (0.33 cm) for the size of panel used.

2. WEIGHT OF DOPED FABRIC

The doped fabric was removed from the panels and three 2 by 4 inch (5.1 by 10.2 cm) pieces were cut by a die from a strip at the center. These cut samples were weighed on a chemical balance in the conditioning room.

3. FLAMMABILITY OF DOPED FABRIC

Methods of determining the flammability of fireproofed fabrics have been discussed by Ramsbottom and Snoad (66), and of plasticizers by Van Heuckeroth.[3] A vertical burning test was employed in each case; however, the cloth was ignited at the bottom by the former investigators, whereas in the work with the plasticizers, the lacquered paper was ignited at the top. In our work a horizontal burning test, which results in rates of burning intermediate between the two vertical tests mentioned above, was preferred because it accentuated any differences in the flammability of the various materials tested. The apparatus used is shown in figure 2 and was developed by C. R. Brown, of the Fire Resistance Section of the National Bureau of Standards. It consists of two parallel steel clamps supported by a steel frame, the distances between the clamps being adjustable. The specimen to be tested is fastened between the clamps and ignited at one end. The time required for the flame front to travel over a given distance as measured along the clamps is recorded with a stop watch and the rate of burning in inches per minute is calculated. Any length of specimen up to 24 inches (61 cm) and any width up to 7 inches (17.8 cm) can be burned in this apparatus. Brown found that no appreciable effect could be noted due to differences in length provided the specimens were well ignited before starting the time record. He also studied the effect of variation in the free width of the specimen held between the clamps and found that, in general, an increase in width causes an increase in the rate of burning. Inasmuch as the specimens 6 inches (15.2 cm) in width burned irregularly and consequently gave greater variations in the results, he recommended that strips 2 inches (5.1 cm) in width be used for this test. It will be noted that this apparatus can also be used for a vertical burning test. This vertical test was used for the experiments on cloth containing fireproofing compounds, which make the fabric practically nonflammable in the horizontal position. To obtain the results presented in this paper, specimens with surfaces 2 inches (5.1 cm) in width for the horizontal test and 1 inch (2.5 cm) in width for the vertical test were exposed between the clamps, the cloth was ignited with a safety match, and the time recorded for the flame front

[3] A. W. Van Heuckeroth, Some properties of lacquer plasticizers in nitrocellulose films and solutions, Am. Paint Varnish Mfrs. Assn. Cir. 383, p. 187 (1931).

to travel 12 inches (30.5 cm) after starts of 2 and 3 inches (5.1 and 7.6 cm), respectively, for the horizontal and vertical positions. The experiments were made in the still air of the laboratory. The fabrics were left in the conditioning room approximately one week after doping before determining their flammability.

III. EXPERIMENTAL WORK

1. RESINS, CASEIN, AND CELLULOSE DERIVATIVES AS DOPE CONSTITUENTS

The flammability and tautness of airplane cloth doped with various natural and synthetic resins, casein, and cellulose derivatives are shown in table 1. These data are summarized from a considerably larger number of experiments on various commercial resins of the types indicated, and the relative flammability of the various chemical types was definitely maintained in the whole series. In applying these materials to the airplane cloth low-boiling solvents were used instead of the usual blend of low-, medium-, and high-boiling solvents, in order to lessen the possibility of the solvent remaining in the film and influencing the rate of burning. Because of the diverse solubilities of the materials studied four different solvents, namely, acetone, ethyl alcohol, benzene, and aqueous ammonia, had to be employed. The five experiments listed at the bottom of table 1 indicate that the use of different solvents did not affect the comparative nature of the results.

TABLE 1.—*Flammability and tautness of airplane cloth doped with natural and synthetic resins, casein, and cellulose derivatives*

Doping material	Solvent	Total weight	Rate of burning	Deflection of tautness meter plunger under 15-oz load
		Oz/sq yd	In./ min	In.
Chlorodiphenyl resin	Acetone	6.2	2.2	Slack
Vinyl chloride resin	do	6.3	3.5	0.140
Casein	Aqueous NH_3	6.1	3.7	.148
Vinyl acetate resin	Acetone	6.0	4.8	Slack
Cellulose acetate	do	5.8	4.8	.097
None		3.9	5.9	
Phthalic acid ester resin	Acetone	6.2	7.2	.229
Rosin-glycerin resin	do	6.2	7.2	.220
Shellac	Ethanol	5.7	7.7	.179
Phenol-formaldehyde resin	Acetone	6.2	7.9	.209
Cumaron resin	do	5.7	8.0	.163
Macassar gum	Ethanol	6.1	9.4	Slack
Modified phenol-formaldehyde resin	Benzene	6.2	9.8	.158
Urea-formaldehyde resin	Acetone	6.0	9.9	Slack
Spar varnish		6.1	10.0	.269
Petroleum hydrocarbon resin	Benzene	5.7	10.2	.193
Manila gum	Ethanol	5.9	10.9	Slack
Cyclohexanone-vinyl resin	Acetone 1 pt, Benzene 1 pt	6.0	14.0	.257
Cellulose nitrate	Acetone	5.9	23.2	.113
Vinyl acetate resin	Acetone	6.1	5.1	.153
Do	Benzene	6.3	5.5	.178
Do	Toluene	6.2	5.1	.183
Do	Ethanol	6.0	4.6	Slack
Do	Ethyl acetate	6.2	5.0	.175

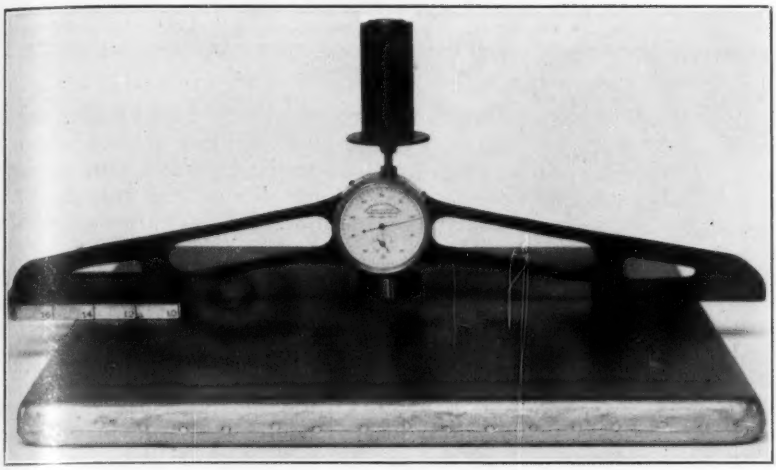

FIGURE 1.—*McGowan tautness meter.*

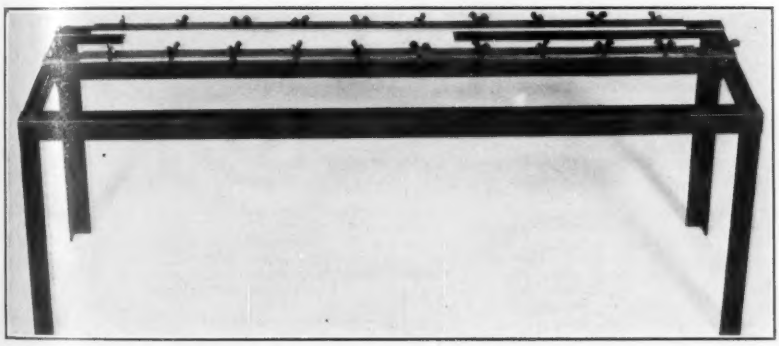

FIGURE 2.—*Brown's apparatus for determining rate of burning.*

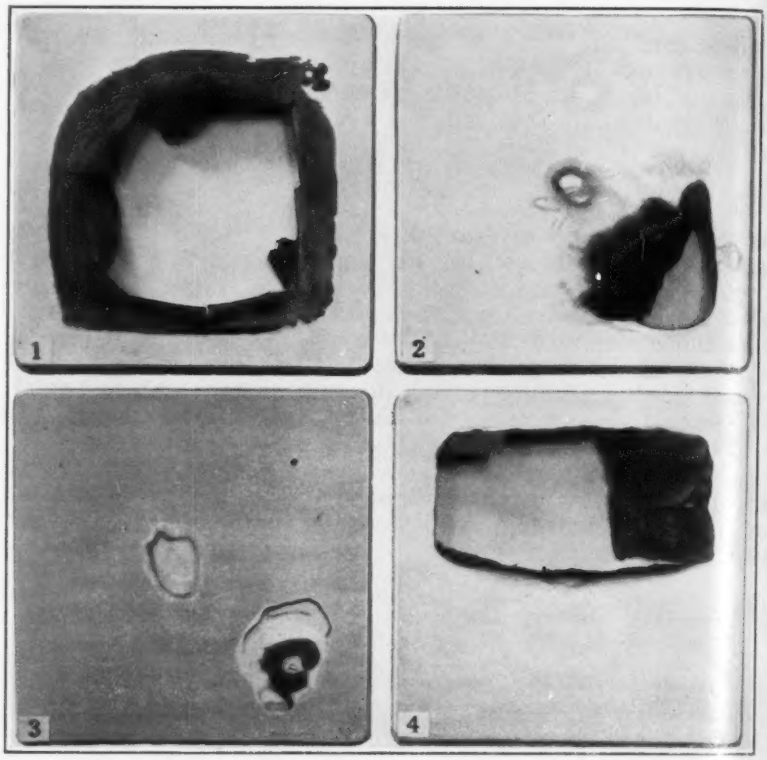

FIGURE 3.—*Flammability tests on doped fabrics.*

Four coats of clear dope and two coats of aluminum pigmented dope were applied to airplane cloth tacked on wooden frames. The square gray areas surrounding the charred doped fabric are the aluminum pigmented surfaces.

1, Untreated airplane cloth doped with cellulose nitrate. The flames spread rapidly when burning gasoline ignited the nitrate doped fabric at the center of the panel.

2, Untreated airplane cloth doped with cellulose acetate. Note the slightly charred area at the center of the panel where burning gasoline did not ignite the acetate doped fabric. When one corner of the panel was cut to expose the cloth, the doped fabric was ignited and burned slowly.

3, Fireproofed airplane cloth doped with cellulose acetate. Burning gasoline did not set fire to the acetate doped fabric with or without exposure of the cloth surface.

4, Fireproofed airplane cloth doped with cellulose nitrate on the upper half of the panel and with cellulose acetate on the lower half. Burning gasoline ignited the nitrate doped fabric, but note that the resultant fire did not ignite the acetate doped fabric.

It will be noted that only three materials yielded a doped fabric which had a greater resistance to burning than cellulose acetate, namely, chlorinated diphenyl resins, vinyl chloride resins, and casein. These resins as well as those which were more flammable than cellulose acetate did not give satisfactory tautness. An occasional panel was secured with vinyl chloride resin which showed good tautness, but this material was not investigated further as chlorinated products, particularly of the aliphatic type, are not believed to be desirable for use on airplane fabrics because of their deteriorating action when exposed to sunlight. It is interesting to note that cellulose acetate burns approximately one-fifth as rapidly as cellulose nitrate, and that in these unplasticized films the tautness obtained with cellulose acetate is greater than that obtained with cellulose nitrate.

2. MIXTURES OF RESINS AND CELLULOSE DERIVATIVES AS AIRPLANE DOPES

The use of mixtures of synthetic resins and cellulose nitrate and acetate for airplane dopes has been suggested in numerous patents. The results of some experiments with such mixtures are presented in table 2. The addition of those resins which are least flammable, such as the chlorinated diphenyl, vinyl acetate, and phthalic acid ester types, to the usual dopes prepared from cellulose derivatives decreased the flammability of the doped fabric somewhat, but also had a very adverse effect on the tautness. In general, a minimum ratio of 3:1 of cellulose nitrate or acetate with these resins is necessary in order to attain satisfactory tautness. The application of the chlorinated diphenyl resin as a surface coating did not appreciably lower the rate of burning of fabrics doped with cellulose nitrate or acetate.

TABLE 2.—*Mixtures of resins and cellulose derivatives as airplane dopes*

Type of cellulose derivative in the dope	Type of resin in the dope	Weight ratio of cellulose derivative to resin	Total weight	Rate of burning	Deflection of tautness-meter plunger under 15-oz load
			Oz/sq yd	In./ min	In.
Acetate	None		6.6	5.0	0.096
Do	Chlorinated diphenyl	1:1	6.4	2.9	.186
Do	do	2:1	6.3	3.8	.157
Do	do	3:1	6.1	4.6	.152
Do	Vinyl acetate	3:1	5.9	5.0	.117
Do	Phthalic acid ester	3:1	5.9	5.8	.109
Nitrate	None		6.6	21.3	.101
Do	Chlorinated diphenyl	1:1	6.9	14.8	.161
Do	do	2:1	6.4	16.6	.169
Do	do	3:1	7.6	22.9	.112
Do	Vinyl acetate	2:1	7.9	14.0	.123
Do	do	3:1	7.7	17.8	.093
Do	Phthalic acid ester	3:1	6.4	20.6	.120

3. FIREPROOFING OF CLOTH

When it became apparent that the problem of developing a fire-resistant doped fabric could not be solved by the addition of non-flammable resins to the cellulosic dopes, or by the complete substitution of resins for the cellulose derivatives in the dope, the course of this investigation was directed toward the production of an airplane fabric doped with cellulose acetate and fireproofed by the addition

of fire-retarding salts. Some experiments were performed on the direct addition to the dope of some inorganic materials of known fireproofing qualities, but this method was largely unsuccessful because of the insolubility of inorganic substances in the organic solvents commonly used in airplane dopes. Furthermore, the cloth underlying the fireproofed film served as a wick to prevent the flame from extinguishing. The problem of fireproofing the fabric before application of the dope was, therefore, considered.

A survey of the literature indicated that the inorganic salts most generally recommended for fireproofing fabrics are ammonium sulphate, ammonium phosphate, and a mixture of boric acid and borax. A bibliography of the recent literature on fireproofing is given at the end of this paper. Ramsbottom and Snoad's (66) investigation included the above-mentioned materials as well as many others, and they concluded that a mixture of 30 percent boric acid and 70 percent borax is one of the most suitable soluble fireproofing agents for cotton fabric. They found that when it is present to the extent of about 6 percent of the weight of the fabric it prevents the propagation of the flame. They also noted the lack of any marked deteriorating effect of this mixture on the cloth. The boric-acid-borax mixture also has the advantages of being nonpoisonous and slightly germicidal.

TABLE 3.—*Fireproofing of cloth.*

Material added to cloth	Increase in weight	Rate of burning	
		Horizontal	Vertical
	Percent	In./min	In./sec
Borax	4.6	No flame spread	0.65
Do	8.8	No flame spread	.66
Boric acid	5.3	3.8	.92
Do	7.4	4.2	1.04
3:7 Boric acid-borax	2.8	3.8	.71
Do	3.7	No flame spread	.57
Do	4.6	No flame spread	No flame spread
Commercial product no. 1	3.2	3.7	1.15
Do	6.0	No flame spread	No flame spread
Commercial product no. 2	4.2	4.1	1.04
Do	4.8	No flame spread	No flame spread
Commercial product no. 3	3.4	No flame spread	.90
Do	5.7	No flame spread	No flame spread
Ammonium borate	4.6	No flame spread	.76
Barium borate	5.4	6.0	.88
Magnesium perborate	7.2	3.3	.74
Sodium acetate	5.5	3.5	No flame spread
Sodium formate	8.8	No flame spread	No flame spread
Triphenyl phosphate	8.6	5.7	1.15
None		5.9	1.15

The results of measurements of the rates of burning of airplane cloth impregnated with boric acid, borax, and a mixture of 30 percent boric acid and 70 percent borax are shown in table 3. They confirm the tests of Ramsbottom and Snoad and indicate that the mixture is efficient in very small amounts, a feature which is particularly desirable for aeronautical use where weight is a predominant factor. The results of tests with other borates, some commercial products, and a few miscellaneous materials are also shown in table 3; none of them was found to be more efficient in fireproofing than the boric-acid-borax mixture.

4. EFFECT OF FIREPROOFING AIRPLANE CLOTH ON THE FIRE RESISTANCE OF THE PRODUCT COVERED WITH CELLULOSIC DOPES

Test results on ordinary and fireproofed airplanes fabrics coated with commercial cellulose nitrate and cellulose acetate dopes are shown in table 4 and figure 3. Ordinary airplane fabric coated with cellulose acetate dope does not ignite readily when lighted matches or cigarettes are dropped on it, even in a fan breeze. Once ignited, however, it burns at a comparatively slow rate without extinguishing itself. Ordinary airplane fabric coated with cellulose nitrate dope is instantly ignited by a lighted safety match dropped on the panel placed in a horizontal position, and is soon completely consumed. The data in table 4 show that satisfactory protection against ignition may be obtained by the application of the boric-acid-borax mixture to the cloth before doping it with cellulose acetate. This doped and fireproofed cloth will not burn 12 inches (30.4 cm) in either a horizontal or vertical position. Furthermore, gasoline (approximately 3 ml) splashed on the horizontal surface and ignited is burned off without setting fire to the doped fabric. The amount of fireproofing mixture required on the cloth is approximately 5 percent of the total weight. It will be noted that one specimen covered with four coats of clear cellulose acetate dope and two coats of aluminum-pigmented cellulose acetate dope, but which contained only about 3.5 percent of the boric-acid-borax mixture, would burn when ignited, whereas a similar panel on which the fireproofing mixture represented 4 percent of the total weight was protected against ignition by lighted match or burning gasoline.

TABLE 4.—*Flammability and tautness of airplane fabric with and without boric-acid-borax mixture when it is doped with cellulose nitrate and cellulose acetate*

Amount of boric acid-borax on the cloth	Doping scheme	Total weight	Rate of burning	Action of burning match on the fabric	Action of burning gasoline on the fabric	Deflection of tautness-meter plunger under 15-oz load
Oz/sq yd		Oz/sq yd	In./min			In.
None	None	3.88	5.9	Ignited	Ignited	
0.31	do	4.19	No flame spread	Charred	Charred	
None	6 coats clear acetate	7.5	4.3	do	Ignited	0.079
0.31	do	7.7	No flame spread	do	Charred	.082
None	4 coats clear acetate 2 coats Al-pigmented acetate	8.5	6.9	do	Ignited	.075
0.31	4 coats clear acetate 2 coats Al-pigmented acetate	8.8	3.1	do	do	.079
0.31	4 coats clear acetate 2 coats Al-pigmented acetate	7.9	No flame spread	do	Charred	.086
None	6 coats clear nitrate	7.3	19.2	Ignited	Ignited	.091
0.31	do	7.4	14.4	do	do	.094
None	4 coats clear nitrate 2 coats Al-pigmented nitrate	8.4	18.2	do	do	.083
0.31	4 coats clear nitrate 2 coats Al-pigmented nitrate	8.7	13.6	do	do	.081
1.3	4 coats clear nitrate 2 coats Al-pigmented nitrate	12.2	3.8	do	do	.072
None	6 coats orange-yellow semi-pigmented nitrate.	7.4	18.9	do	do	.099
0.31	6 coats orange-yellow semi-pigmented nitrate.	8.0	12.9	do	do	.096
None	4 coats clear acetate 2 coats clear nitrate	6.8	9.4	do	do	.098
None	4 coats clear acetate 2 coats Al-pigmented nitrate	7.5	13.0	do	do	.099
None	4 coats clear nitrate 2 coats clear acetate	7.0	15.9	do	do	.105
None	4 coats clear nitrate 2 coats Al-pigmented acetate	8.0	19.5	do	do	.097

The greater ease of ignition of the cellulose nitrate coatings can be ascribed to the lower temperatures causing decomposition and ignition. The basic difference in decomposition and burning of cellulose nitrate and cellulose acetate is that the former burns independently of an exterior source of oxygen supply to an extent permitting partial combustion of the gases formed. Although it is preferable to have a combination which is self-extinguishing, such as can be obtained by fireproofing the airplane cloth before doping with cellulose acetate, if one is choosing between two materials which will support combustion, it is important to have the ignition temperature as high as possible. Various definitions and methods of measurement of ignition temperature have been proposed by investigators in this field. The National Bureau of Standards has not adopted or endorsed as standard any definition or method of measurement of ignition temperature. There is general agreement in the literature that the ignition temperature of cellulose nitrate is approximately 200° C below that of cellulose acetate. Thus, the values found for the ignition temperature of cellulose nitrate products by Barr,[4] Brown,[5] and Nuckolls[6] are respectively 200, 135, and 149° C, whereas their values for cellulose acetate products are 380, 314, and 371 to 427° C, respectively. When it is considered that the temperature of ordinary incandescent lights, steam pipes, and lighted cigarettes and matches exceeds 149° C,[6] the constant risk of fire on an airplane doped with cellulose nitrate is readily apparent.

The dopes used in the experiments described in table 4 were commercial products containing only small amounts of high-boiling solvents. Some experiments were also performed with a cellulose acetate dope prepared in the laboratory according to the British Standard Reference Dope formula,[7] except that ethyl acetate was substituted for benzene, and ethyl lactate for benzyl alcohol, to yield the following percentage composition:

Cellulose acetate	7.1
Triphenyl phosphate	1.1
Acetone	46.8
Ethyl acetate	20.0
Ethyl alcohol	20.0
Ethyl lactate	5.0

The results were similar to those obtained with the commercial cellulose acetate dope. It is recognized that a higher percentage of high-boiling solvents is required to permit satisfactory doping operations at relative humidities of 65 percent or higher. The retention of high-boiling solvent in the cellulose acetate film or the substitution of a flammable plasticizer for the nonflammable triphenyl phosphate would make the doped fabric considerably less fire-resistant than were the fabrics described in table 4. It is planned to determine the effect of larger percentages of high-boiling solvents and of various plasticizers on the fire resistance of the doped fabric.

[4] G. Barr, The Inflammability of Doped Fabrics, Advisory Comm. for Aeronautics, Repts. and Mem. 573 (1919).

[5] C. R. Brown, Tests of Stability at Elevated Temperatures of Nitrocellulose X-ray Film, Proc. of a Board of the Chem. Warfare Service (re Cleveland Clinic Disaster May 15, 1929), p. 46 (1929); compare also p. 37. The Determination of the Ignition Temperatures of Solid Materials, Doctoral Dissertation, Catholic University of America, Washington, D. C. (1934). The ignition temperatures of solid materials, Quart. Nat. Fire Protect. Assn. **28**, 135 (1934). Compare H. N. Stokes and H. C. P. Weber, Tech. Pap. BS T98 (1917).

[6] A. H. Nuckolls, Cellulose nitrate and acetate film, Quart. Nat. Fire Protect. Assn. **23**, 236 (1930). H. E. Hofmann, and E. W. Reid, Cellulose acetate lacquers, Ind. Eng. Chem. **21**, 955 (1929).

5. EFFECT OF MIXED CELLULOSE NITRATE AND CELLULOSE ACETATE DOPING SCHEMES ON THE FIRE RESISTANCE OF THE DOPED FABRIC

The use of mixtures of cellulose acetate and cellulose nitrate for airplane dopes has been proposed in various patents. Recent army and navy specifications for the application of dopes to fabric surfaces of aircraft have permitted the application of base coats of clear cellulose acetate dope, when followed by pigmented cellulose nitrate dope. The last four experiments shown in table 4 indicate that the fire protection offered by cellulose acetate dope is largely lost if cellulose nitrate dope is used for the outer coats. To secure the greater protection afforded by cellulose acetate, its use should be specified for the entire doping scheme.

IV. DISCUSSION OF RESULTS

A thorough study of the use of cellulose nitrate and cellulose acetate as airplane dopes was undertaken by the United States Government during the period of the war. Published reports indicate that cellulose nitrate was considered undesirable for use at the "front" because of its flammability, and that cellulose acetate dope was preferred and, in general, prescribed for airplanes to be used in the zone of fire. Considering the comparative meagerness of the technological information concerning cellulose acetate in that period, its preferential use for doping airplanes is surprising and is indicative of the attitude of the wartime aeronautical engineers toward the fire hazard of cellulose nitrate dope. After the war the development of cellulose nitrate lacquers received a remarkable impetus in the need of a low-cost, quick-drying coating material for many industrial purposes, notably automobile bodies, and rapid technical advances were made. New solvents were developed for cellulose nitrate, the common solvents were reduced in price by improvements in manufacturing methods and volume production, and the spraying process was perfected. As a result the improved cellulose nitrate lacquers, with a few changes to make them suitable for doping airplane cloth, gradually replaced the less hazardous cellulose acetate dope which was technically dead in that post-war period. Today, however, the technical position of cellulose acetate has been altered. The rapid increase in the use of motion-picture and X-ray films made from cellulose nitrate was accompanied by a number of serious conflagrations, which centered attention on the desirability of a relatively nonflammable film prepared from cellulose acetate. This acted as a stimulus to research on the production of cellulose acetate and its solvents, and resulted in a rapid growth of the manufacture of safety film and cellulose acetate plastics. Cellulose acetate dopes are, therefore, now only moderately more expensive than cellulose nitrate dopes. When it is considered that the cost of the dope is much less than 1 percent of the total cost of an airplane, this difference in price of the two dopes becomes insignificant as compared with the potential loss resulting from the destruction of the airplane by the accidental ignition of the fabric doped with the very flammable cellulose nitrate.

It has been stated that fabric doped with cellulose acetate temporarily loses its tautness on long-continued exposure to a humid atmosphere. Preliminary experiments in this laboratory have indicated

that this is not necessarily true of all cellulose acetate dopes. Sheppard and Newsome[8] have observed that esterification of the hydroxyl groups of cellulose with acetic acid decreases the hygroscopicity of the material. It is probable that any slackening off of the doped fabric is closely associated with the hygroscopic nature of the plasticizer used. The loss of tautness observed with the cellulose acetate dopes of the wartime period may also be ascribable to the hydrolysis of the cellulose acetate by the acid liberated by the decomposition of chlorinated solvents (6) generally employed at that time. These solvents are no longer permitted in airplane dopes for service use in this country. The fact that cellulose acetate dope is required and the very flammable cellulose nitrate excluded from use on service airplanes by the French is evidence that satisfactory performance can be attained with cellulose acetate dope. Furthermore cellulose acetate is specified and found to be satisfactory for doping the outer cover of airships in this country. The further precaution of fireproofing the cloth, with the small increment of weight found to be necessary in this investigation might well be considered for the large dirigibles, the destruction of which by fire represents a large economic loss.

Further work on the permanence of the fire protection which would be afforded by the use of boric-acid-borax mixture on airplane wings and fuselage is necessary. There is every reason to believe that the aluminum-pigmented cellulose acetate coating would prevent for long periods the removal of the soluble salts on exposure to atmospheric weathering. The much greater durability of cellulose acetate over that of cellulose nitrate on weathering was well established during the period of the war (3), and by subsequent experimental work with the two materials on exposure to ultraviolet light. The lack of any marked deteriorating action of the boric-acid-borax mixture on cotton cloth, noted by Ramsbottom and Snoad, has already been mentioned. In view of the necessity of concentrating many airplanes in a limited space on airplane carriers, on which there exists increased danger of the ignition of cellulose nitrate by flying sparks or by spontaneous decomposition due to storage close to hot pipes or other sources of heat, it is believed that serious consideration should be given to the use of fireproofed doped fabric on aircraft, and that the investigation of such materials both in the laboratory and on test airplanes should be actively pursued.

V. SUMMARY AND CONCLUSIONS

1. The comparative flammability and tautness of fabric doped with natural and synthetic resins have been determined. The resins studied do not tighten the fabric sufficiently to be satisfactory as airplane dopes.

2. The use of mixtures of synthetic resins and cellulose derivatives as airplane dopes has been investigated. In general, a 3:1 ratio of cellulose derivative to resin is necessary to attain satisfactory tautness. In this proportion even the least flammable synthetic resins do not markedly improve the fire-resistance of the doped fabric.

[8] S. E. Sheppard and P. T. Newsome. The sorption of water vapor by cellulose and its derivatives. J. Phys. Chem. **33**, 1817 (1929).

3. No method has been found to fireproof airplane fabric doped with cellulose nitrate and maintain satisfactory tautness and weight requirements.

4. An airplane covering with very good resistance to ignition may be obtained by the application of a 3:7 boric-acid-borax mixture to airplane cloth and subsequently doping it with cellulose acetate. This doped and fireproofed cloth, containing approximately 5 percent of the boric-acid-borax mixture by weight, will not burn in a horizontal or vertical position and is not ignited by lighted matches or burning gasoline.

VI. BIBLIOGRAPHY

1. AIRPLANE FINISHING

(1) Anonymous, Report of the Advisory Committee on Aeronautics. India Rubber J. **45,** 1344 (1913).
(2) G. Hubener, Balloon and airplane materials. Kunststoffe **3,** 141, 164, 189, 207, 344, 364, 385, 407 (1913).
(3) G. J. Esselen, Jr., Airplane dopes. Ind. Eng. Chem. **10,** 135 (1918).
(4) Alice Hamilton, Dope poisoning in the making of airplanes. Monthly Rev. U. S. Bureau Labor Statistics **6,** 289 (1918).
(5) W. H. Smith, Airplane dopes and doping. Nat. Advisory Comm. Aeronaut. Rept. 38, (1918).
(5a) W. S. Smith, Nonpoisonous dope. Chem. Trade J. **63,** 44 (1918).
(6) G. Barr and L. L. Bircumshaw, Cellulose acetate. Advisory Comm. Aeronaut. Repts. and Mem. 303; compare Repts. and Mem. 318 and 573.
(7) W. D. Milne, Fire hazard in airplane manufacture. Nat. Fire Protect. Assn. Quart. p. 345 (April 1919).
(8) A. Rusch, Jr., Aviation textiles and chemistry. Textile World J. **56,** 363 (1919).
(9) A. W. Chapman, Chemistry of aeronautics. Chem. Age (London) **2,** 438 (1920).
(10) M. Deschiens, Cellulose acetate and its industrial uses. Chimie & Industrie **3,** 591 (1920).
(11) M. Deschiens, Airplane dopes. Rev. Prod. Chim. **23,** 177 (1920).
(12) M. Deschiens, Dope manufacture. Chem. Trade J. **67,** 603 (1920).
(13) H. J. H. Fenton and A. J. Berry, Cellulose acetate. Proc. Cambridge Phil. Soc. **20,** 16 (1920).
(14) A. Fuchs, Materials and dopes for airplanes. Chimie & Industrie **3,** 167 (1920).
(15) H. A. Gardner, An emollient for skin protection in the dope and varnish using industries. Paint Mfrs. Assn. U. S. Cir. 91 (May 1920).
(16) G. W. C. Kaye, British Standard of Reference for Aircraft Dope and Protective Covering. (Crosby Lockwood and Son, London, 1918).
(17) M. Deschiens, Airplane dopes. Rev. Prod. Chim. **24,** 3 (1921).
(18) P. Drinker, European practice in cellulose acetate and dopes during the war. Ind. Eng. Chem. **13,** 831 (1921).
(19) A. W. Judge, Aircraft and Automobile Materials of Construction. **II.** Nonferrous and Organic Materials. (Sir Isaac Pitman and Sons, Ltd., London, 1921).
(20) J. R. S. Cochrane, Airplane dopes. Materials, Plant, and Process for Production of Cellulose Acetate. Commonwealth Australia Munitions Supply Board Tech. Repts. (1921–22).
(21) H. W. van Urk, Poisoning symptoms from the solvents of airplane lacquers. Pharm. Weekblad **60,** 293 (1923).
(22) A. Feil, Occupational poisoning with tetrachloroethane. Chimie & Industrie, Special no., page 763 (May 1924).
(23) M. Deschiens, Aviation dopes or varnishes. J. Soc. Chem. Ind., Chem. and Ind. Rev. **44,** 902 (1925).
(24) H. Hepworth, Industrial nitrocellulose products. Ind. Chemist **1,** 323 (1925).
(25) M. Deschiens, Airplane dopes. Chimie & Industrie **15,** 18 (1926).

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(26) H. A. Gardner, Durability of airplane doping and varnishing systems. A study of cellulose acetate and cellulose nitrate tautening and proofing schemes for fabric surfaces. Paint Mfrs. Assn. U. S. Cir. 274, 61 (1926).
(27) A. Hutin, Mixed dopes from cellulose acetate and rubber. Rev. gén. mat. plastiques, **2,** 308 (1926).
(28) H. T. S. Britton, Cellulose acetates for aero dopes. Ind. Chemist **3,** 59 (1927).
(29) H. T. S. Britton, Aero dopes and varnishes. Ind. Chemist **3,** 116 (1927).
(30) K. Atsuki and R. Shinoda, Composition of cellulose acetate lacquer for airplane dope. Rept. Aeronaut. Research Inst., Tokyo Imp. Univ. **3,** 49 (1928).
(31) R. C. Martin, Finishing modern aircraft. Chem. Met. Eng. **35,** 404 (1928).
(32) M. C. Roberts, Modern airplane finishing, Ind. Finishing **4,** 29 (Sept. 1928).
(33) D. M. Liddell, Chemicals in aviation. Chem. Markets **25,** 249 (1929).
(34) C. J. Staud, Technology of cellulose acetate. Its relation to plasticizers and solvents. Paint, Oil, Chem. Rev. **88,** no. 19, 9 (1929).
(35) G. E. Walker, How chemical engineering has improved aircraft. Chem. Met. Eng. **36,** 348 (1929).
(36) Anonymous, Report of Fact-Finding Committee on Control of Airplane Hangar Fires by Automatic Application of Water. Aeronautics Branch, U. S. Department of Commerce (September 1930).
(37) T. Araki and T. Nagamote, Ethylcellulose dope. J. Soc. Chem. Ind. Japan, **33** (supplemental binding) 382 (1930).
(38) H. A. Backus, Specifications and materials control for aircraft construction. Proc. Am. Soc. Testing Materials **30,** part 2, 109 (1930).
(39) H. A. Gardner, Notes on aircraft finishes. Proc. Am. Soc. Testing Materials **30,** part 2, 68 (1930).
(40) T. Lyons, Metals used in airplane construction. Monthly Rev. Am. Electroplaters' Soc. **18,** no. 9, 26 (1931).
(41) J. L. McCloud, Requirements of airplane coatings. Ind. Eng. Chem. **23,** 1334 (1931).
(42) O. Merz, Paints for aircraft and their testing. Farben-Ztg. **36,** 2156, 2197 (1931).
(43) T. Araki and T. Nagamote, Benzylcellulose dope. J. Soc. Chem. Ind. Japan, **35** (supplemental binding) 68 (1932).
(44) R. A. Denne, The problem of fire in aircraft. Aircraft Eng. **4,** 98 (1932).
(45) E. K. O. Schmidt, Preservation of airplane fabrics. Farben-Chem. **3,** 165, 209 (1932).
(46) H. T. Tizard, Chemical engineering and the aircraft industry. Trans. Inst. Chem. Engrs. **10,** 87 (1932).
(47) G. M. Kline, Estimation of tautness of doped fabrics. Am. Paint Varnish Mfrs. Assn. Cir. 443, 266 (1933).
(48) P. Meunier and A. Lucain, Properties and application of benzylcellulose. Rev. gén. mat. plastiques **9,** 127 (1933).
(49) O. Merz, Paint materials for airplane construction and their testing. Malyarnoe Delo **1932,** no. 516, 31. Compare Chem. Zentr. **1933,** I, 2182.
(50) C. F. Nagel, Jr., and G. O. Hoglund, Developments in aluminum alloys in relation to economies in aircraft construction. Trans. Am. Soc. Mech. Engrs. (Aeronaut. Eng.) **5,** 75 (1933).
(51) M. R. Whitmore, Aircraft finishing, Ind. Eng. Chem. **25,** 19 (1933).
(52) C. A. Young, Dope poisoning as a potential hazard in spray-coating airplane wings. U. S. Naval Med. Bul. **31,** 63 (1933).
(53) J. J. A. Gilmore, Airplane doping schemes. Aircraft Eng. **6,** 161 (1934).
(54) R. Lecoeuvre, Repair and upkeep of metal hulls and floats for hydroplanes. Chimie & Industrie, Special no., page 547 (1934).
(55) M. W. Mason, Aircraft finishing. Ind. Finishing **10,** no. 5, 18; no. 6, 16; no. 7, 16; no. 8, 32 (1934).
(56) W. Mutchler, Weathering of aluminum alloy sheet materials used in aircraft. Nat. Advisory Comm. Aeronaut. Rept. 490 (1934).
(57) E. K. O. Schmidt, Determining the tautness of airplane dopes. Farben-Ztg. **39,** 1049 (1934).
(58) R. Stratta, Adhesion of a film of cellulose acetate to airplane fabric. Industria chimica **9,** 319 (1934)
(59) G. M. Kline, Moisture relations of aircraft fabrics. J. Research NBS **14,** 67 (1935) RP758.

(60) G. M. Kline, Absorption of moisture by aeronautical textiles. Am. Dyestuff Rept. **24**, 4 (1935).

2. FIREPROOFING

(61) Anonymous, The manufacture of fireproof coating materials. Farbe u. Lack **1926**, 456.
(62) A. Eichengrun, Chemical protection against fire. Z. angew. Chem. **42**, 214 (1929).
(63) C. O. Clark, Fabric proofing. Textile Weekly **4**, 696 (1930).
(64) F. Grove-Palmer, Fire-resisting rayon goods. Am. Dyestuff Reptr. **19**, 715 (1930).
(65) G. M. Hunt, T. R. Truax, and C. A. Harrison, Experiments in fireproofing wood. Proc. Am. Wood-Preservers' Assn. **1930**, 130, 159; **1931**, 104; **1932**, 71; **1933**, 107.
(66) J. E. Ramsbottom and A. W. Snoad, Fireproofing of Fabrics. Dept. Sci. Ind. Research, Second Report of Fabrics Coordinating Research Comm. page 16 (1930).
(67) R. Chesneau, Fireproofing of cloth. Bul. soc. ind. Rouen **60**, 265 (1932).
(68) K. Micksch, Flame protectives for rayon. Kunstseide **14**, 64 (1932).
(69) F. I. Sadov and P. V. Sterlov, Fireproofing of fabrics. Za. Rek. Textiln. Prom. **11**, 39 (1932). Compare Chimie & Industrie **28**, 668 (1932).
(70) C. G. Schwalbe and K. Berling, New cheap fire-protecting material for wood. Chem-Ztg. **56**, 909 (1932).
(71) H. Stadlinger, Chemical fireproofing agents. Synthetic and Applied Finishes **3**, 91 (1932).
(72) R. Chesneau, The flame-proofing of textiles. Textile Colorist **55**, 375 (1933).
(73) W. F. Brosnan, Fireproofed textiles. Textile World **84**, 2399 (1934).
(74) E. Kunze, Air defense and fire-protective paints. Farbe u. Lack **1934**, 134.
(75) L. P. Michel, Permanent fireproofing of fabrics. Tiba **12**, 3 (1934).

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GOLD-COBALT RESISTANCE ALLOYS

By James L. Thomas

ABSTRACT

Gold-cobalt alloys containing 0.75 to 5 percent of cobalt have been prepared and investigated to determine if they are suitable for use in the construction of electrical resistance standards. The temperature coefficient of electrical resistance of the alloys containing from 1.5 to 2.5 percent of cobalt is small at room temperatures, but the thermoelectric power of the alloys against copper is large. These alloys were found to be inferior to gold-chromium alloys of about the same proportions.

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I. INTRODUCTION

It has been found by Linde [1] that the electrical resistivity of gold is greatly increased by the addition of a small percentage of cobalt and at the same time its temperature coefficient of resistance is greatly decreased. Extrapolating his data, he predicted that 2 percent by weight of cobalt in gold would give an alloy with a zero temperature coefficient at laboratory temperatures. In order to determine if such alloys were suitable for use in the construction of electrical resistance standards, gold-cobalt alloys containing from 0.75 to 5 percent of cobalt have been prepared at this Bureau and their electrical properties investigated. This investigation was abandoned before completion as it was soon decided that the gold-cobalt alloys were inferior to gold-chromium alloys, which were recently described in this journal.[2] However, the data obtained were thought to be of sufficient interest to justify their publication.

II. PREPARATION OF GOLD-COBALT ALLOYS

The alloys were prepared by melting the gold and cobalt together under borax, in a graphite crucible, by means of an induction furnace. The alloys were heated to about 1,200° C and then poured into a graphite mold. It was found that the two metals did not mix very readily; so in each case the alloys were remelted and again poured into the graphite molds.

[1] J. O. Linde, Ann. Physik **402**, 52 (1931); **407**, 219 (1932).
[2] J. L. Thomas, J. Research NBS **13**, 681 (1934) RP737.

The ingots were first hot-forged into the form of rods 5 or 6 mm square. They were then cold-rolled and swaged to a diameter of 0.75 mm, after which they were drawn down to a diameter of about 0.4 mm. through sapphire dies. The material was annealed four or five times during the rolling and swaging, but it was not annealed during the drawing.

Seven of these gold-cobalt alloys were prepared and investigated. They contained from 0.75 to 5 percent of cobalt by weight, as determined by chemical analyses. Little cobalt was lost during melting and the chemical analyses checked very well with the composition as calculated from the ingredients used. The characteristics of these alloys are given in the following sections.

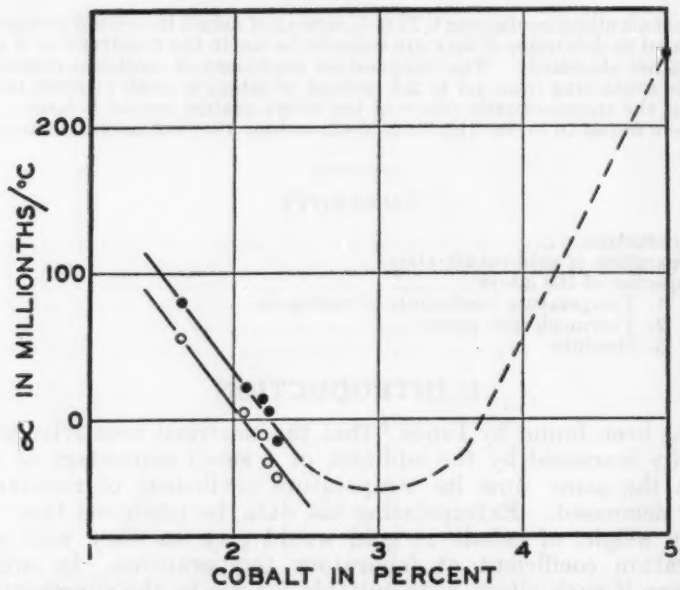

FIGURE 1.—*Temperature coefficients of resistance of gold-cobalt alloys.*
Lower curve is for hard-drawn wire, while upper curve is for wire baked 18 hours at 140° C.

III. PROPERTIES OF THE ALLOYS

1. TEMPERATURE COEFFICIENTS OF RESISTANCE

Ten-ohm coils were constructed of 0.4-mm wire of each of the 7 gold-cobalt alloys. The wire was wound on silk-insulated brass tubes, spaced with silk thread, and the temperature coefficients of resistance were measured. The coils were then shellacked and baked in air at 140° C for 18 hours, after which the temperature coefficients were again measured.

To determine the temperature coefficients, the resistances of the coils were measured at 30 and 40° C. The temperature-resistance curves were not exactly linear, but for the purpose of this investigation it seemed sufficient to determine the temperature coefficient by dividing one-tenth of the change in resistance as the temperature was changed from 40 to 30 ° C by the resistance at 30° C. The tempera-

ture coefficient as determined in this way will be designated by α. The curves of figure 1 show how the temperature coefficient depends upon the cobalt content for alloys containing 1.5 to 5 percent of cobalt. The lower curve is for the unbaked coils while the upper curve is for the coils after baking for 18 hours at 140° C.

Figure 1 shows that for coils baked at 140° C for 18 hours a zero value for α is obtained with an alloy containing about 2.2 percent cobalt. A second alloy containing a somewhat larger proportion of cobalt will also have a zero value of α. This was shown by the fact that the alloy containing 5 percent of cobalt had a positive value for α.

The resistivity of the gold-cobalt alloys at about 25° C is shown in figure 2. The fact that there is a considerable scattering of the points

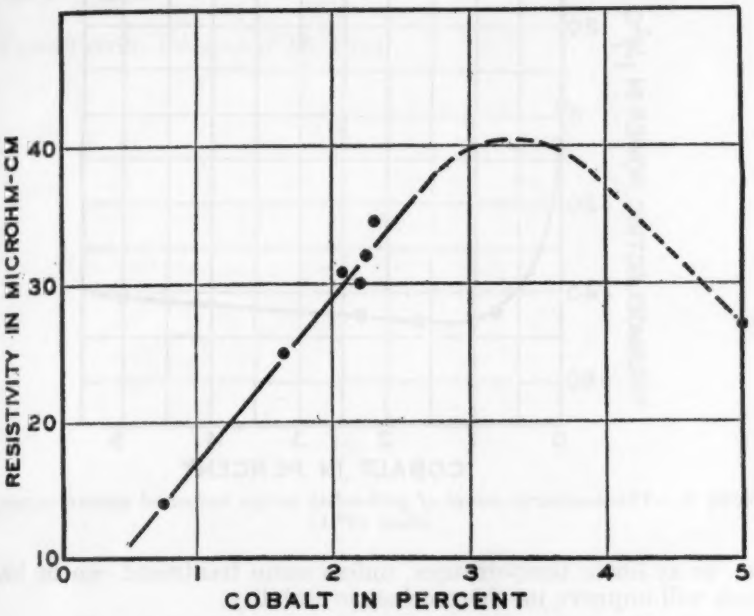

FIGURE 2.—*Resistivity of gold-cobalt alloys at about 25° C.*

would suggest that the components were not perfectly mixed, and that the alloys were therefore not uniform.

2. THERMOELECTRIC POWER

The thermoelectric powers of several of the gold-cobalt alloys against copper were determined by measuring the electromotive force of a couple having one end in an ice bath and the other in an oil bath at about 25° C. The results obtained are shown in figure 3. From this figure it is seen that a maximum (numerically) thermoelectric power against copper of about 47 microvolts per degree centigrade is obtained with about 1 percent by weight of cobalt. With the usual convention [3] the sign of this thermoelectric power is negative. While

[3] Smithsonian Physical Tables, Seventh revised edition, page 317 (1927).

the first 1 percent of cobalt makes a very large change in the thermoelectric power, additional cobalt has comparatively little effect.

The large thermoelectric power of this alloy against copper suggested that it might be used as a thermocouple material. A wire of the 0.75-percent alloy was annealed in air for a short time at 600° C. Measurements of the electromotive force against platinum were made after this annealing, and after two additional heatings in air, each for 7 hours at 350° C. The electromotive force decreased with continued annealing, giving no indication of approaching a steady value. The usefulness of gold-cobalt alloys in thermocouples is therefore probably limited to the measurement of temperatures at or near room tempera-

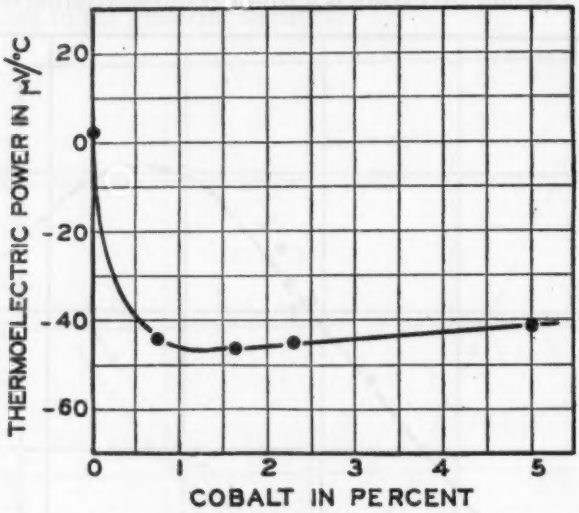

FIGURE 3.—*Thermoelectric power of gold-cobalt alloys measured against copper, at about 15° C.*

ture, or at lower temperatures, unless some treatment can be found which will improve its thermoelectric stability.

TABLE 1.—*Data on resistance coils*

Items	Coil no. 1	Coil no. 2
Percentage of cobalt	2.2	2.3
Baking temperature, °C	140	140
Time of baking, hours	48	48
α in millionths/°C	30	−1
Date (1934)	Resistance (in ohms) at 25° C	
	Coil no. 1	Coil no. 2
Oct. 4	9.99733	9.99872
Oct. 6	9.99737	9.99871
Oct. 9	9.99738	9.99867
Oct. 17	9.99735	9.99861
Oct. 26	9.99734	9.99858
Nov. 16	9.99734	9.99857
Dec. 5	9.99733	9.99854

3. STABILITY

The stability of the electrical resistance of two coils of wire made of the gold-cobalt alloys was determined. One of the coils was very satisfactory, while the other decreased in resistance with time, with little indication of approaching a steady value. Table 1 shows the data obtained for these two coils. The values of α given for these coils are larger than those shown in figure 1, as the coils were given additional baking before determining the stability. No explanation can be given of the difference in the performance of these coils. It does not seem that it can be attributed to the difference in the composition of the alloys, and the construction and baking were the same for the two coils.

WASHINGTON, December 18, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP790

Part of Journal of Research of the National Bureau of Standards, Volume 14, May 1935

A METHOD FOR FINDING THE ROOTS OF THE EQUATION $f(x)=0$ WHERE f IS ANALYTIC

By Charles L. Critchfield and John Beek, Jr.

ABSTRACT

An expression is derived giving the roots of equations involving only functions which may be expressed in power series. The expression takes the form $x_n=x_o-\frac{U_{n-1}}{U_n}$, where $\sum_{i=0}^{n}(-1)^i a_i U_{n-i}=0$ and $a_r\equiv\frac{f^{(r)}(x_o)}{r!f(x_o)}$, and x_n approaches the value of the root as n increases without bound. Methods are given for the treatment of certain special forms. An example is given of the application of the method to the calculation of real roots.

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I. INTRODUCTION

The use of recursion formulas in evaluating roots of equations was described by Euler.[1] Since that time the formulas and the related determinants have been presented by various authors,[2] the most recent example being the series involving determinants developed by E. T. Whittaker.[3] However, three of the quantities necessary to the evaluation of the r^{th} term of this series are sufficient to determine the sum of the first r terms, so that the series form is not the most convenient one for calculation. In the present paper the recursion formulas are developed in an elementary way, and put in a form which is convenient for calculation.

[1] Introductio in Analysii Infinitorum, **1**, chap. 17 (1748), or the translation by J. B. Labey, p. 257 (Paris, 1796).
[2] F. Cajori, A History of Mathematics, p. 227. (McMillan, London, 1919.)
[3] Proc. Edinburgh Math. Soc. **36**, 103 (1918), or Whittaker and Robinson, Calculus of Observations, p. 120. (Blackie and Son, London, 1924.)

II. DERIVATION OF EQUATIONS

Required the value of x, which is a root of the equation $f(x)=0$, where $f(x)$ is analytic in the neighborhood of x. Then if an arbitrary approximation to x, x_0, lies in the neighborhood of x the function $f(x)$ is given by the series

$$f(x)=a_0+a_1(\Delta x)+\frac{a_2}{2!}(\Delta x)^2+ \ldots . +\frac{a_r}{r!}(\Delta x)^r+ \ldots \ldots \quad (1)$$

where the coefficients $a_r \equiv f^{(r)}(x_0)$ are given and $\Delta x \equiv x-x_0$.

Define

$$g_n(x) \equiv 1+b_{n,1}(\Delta x)+\frac{b_{n,2}}{2!}(\Delta x)^2+ \ldots . +\frac{b_{n,n-1}}{(n-1)!}(\Delta x)^{n-1} \quad (2)$$

where the $n-1$ constants $b_{n,1}, b_{n,2}, \ldots, b_{n,n-1}$ are so chosen that $n-1$ consecutive derivatives (beginning with the second) of the function $\varphi_n(x)$ vanish at x_0, where

$$\varphi_n(x) \equiv f(x)g_n(x)=\varphi_n(x_0)+(\Delta x)\varphi_n'(x_0)+\frac{(\Delta x)^{n+1}}{(n+1)!}\varphi_n^{(n+1)}(x_0)+ \frac{(\Delta x)^{n+2}}{(n+2)!}\varphi_n^{(n+2)}(x_0)+ \ldots . \quad (3)$$

Then

$$\left.\begin{aligned}
&\varphi_n'(x_0)=a_1+a_0b_{n,1}\\
&\varphi_n''(x_0)=0=a_2+2a_1b_{n,1}+a_0b_{n,2}\\
&\varphi_n'''(x_0)=0=a_3+3a_2b_{n,1}+3a_1b_{n,2}+a_0b_{n,3}\\
&\quad . \quad . \quad . \quad .\\
&\quad . \quad . \quad . \quad .\\
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&\varphi_n^{(r)}(x_0)=0=a_r+\binom{r}{1}a_{r-1}b_{n,1}+ \ldots \ldots \ldots +\binom{r}{r-1}a_1b_{n,r-1}+a_ob_{n,r}\\
&\quad . \quad . \quad . \quad .\\
&\quad . \quad . \quad . \quad .\\
&\quad . \quad . \quad . \quad .\\
&\quad . \quad . \quad . \quad .\\
&\varphi_n^{(n-1)}(x_0)=0=a_{n-1}+\binom{n-1}{1}a_{n-2}b_{n,1}+ \ldots +\binom{n-1}{n-2}a_1b_{n,n-2}+a_0b_{n,n-1}\\
&\varphi_n^{(n)}(x_0)=0=a_n+\binom{n}{1}a_{n-1}b_{n,1}+ \ldots +\binom{n}{n-2}a_2b_{n,n-2}+\binom{n}{n-1}a_1b_{n,n-1}
\end{aligned}\right\} \quad (4)$$

The symbol $\binom{r}{i}$ is used to represent the number of combinations of r things taken i at a time.

The equations 4 may be solved for $\varphi_n'(x_0)$, with the result

$$\varphi_n'(x_0)=\frac{D_n}{A_n} \quad (5)$$

where A_n is the cofactor of a_1 in the determinant of the n^{th} order having for the element of the r^{th} row and c^{th} column $\binom{r}{c-1}a_{r-c+1}$. The determinant may be written

$$D_n \equiv \begin{vmatrix} a_1 & a_0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ a_2 & 2a_1 & a_0 & \cdots & 0 & \cdots & 0 & 0 \\ a_3 & 3a_2 & 3a_1 & \cdots & 0 & \cdots & 0 & 0 \\ a_4 & 4a_3 & 6a_2 & \cdots & 0 & \cdots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ a_r & \binom{r}{1}a_{r-1} & \binom{r}{2}a_{r-2} & \binom{r}{c-1}a_{r-c+1} & \cdots & & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & & \cdot & \cdot \\ a_{n-1} & \binom{n-1}{1}a_{n-2} & \binom{n-1}{2}a_{n-3} & \binom{n-1}{c-1}a_{n-c} & \cdots & \binom{n-1}{n-2}a_1 & & a_0 \\ a_n & \binom{n}{1}a_{n-1} & \binom{n}{2}a_{n-2} & \binom{n}{c-1}a_{n-c+1} & \cdots & \binom{n}{n-2}a_2 & \binom{n}{n-1}a_1 & \end{vmatrix}$$

Equation 3 may be put in the form

$$\varphi_n(x) = a_0 + (\Delta x)\varphi_n'(x_0) + R_n, \tag{6}$$

where R_n represents the sum of the terms containing powers of Δx higher than the n^{th}. Solving equation 6 for Δx and putting $\varphi_n(x)=0$, we have

$$\Delta x = -\frac{a_0 + R_n}{\varphi_n'(x_0)} \tag{7}$$

We may write

$$\Delta_n x \equiv -\frac{a_0}{\varphi_n'(x_0)} \tag{8}$$

Then, as $\lim_{n\to\infty} R_n = 0$, $\lim_{n\to\infty} \Delta_n x = \Delta x$.

From equations 8 and 5 we have

$$\Delta_n x = -\frac{a_0 A_n}{D_n} \tag{9}$$

It may be shown that $A_n = nD_{n-1}$. Multiplying each element of D_{n-1} by $\frac{r+1}{c}$, the element becomes $\binom{r+1}{c}a_{r-c+1}$, which is the element of A_n. In this process D_{n-1} is multiplied by $\frac{n!}{(n-1)!}$, or n. Thus

$$A_n = nD_{n-1} \tag{10}$$

Then from equations 9 and 10

$$\Delta_n x = -\frac{n a_0 D_{n-1}}{D_n} \tag{11}$$

A recursion formula for D_n may be obtained by expanding it on the elements of the n^{th} row. The result is

$$\sum_{i=0}^{n} (-1)^i \binom{n}{i} a_i a_0^{i-1} D_{n-i} = 0 \tag{12}$$

This may be simplified by writing $U_r \equiv \frac{D_r}{r! a_0^r}$ and $\alpha_r \equiv \frac{a_r}{r! a_0}$.

Equation 12 then becomes

$$\sum_{i=0}^{n} (-1)^i \alpha_i U_{n-i} = 0 \quad (n = 1, 2, 3, \ldots .) \tag{13}$$

Now equation 11 may be written

$$\Delta_n x = -\frac{U_{n-1}}{U_n} \tag{14}$$

Clearly $U_0 = D_0 = 1$, in this development, but in general the value of U_0 may be chosen arbitrarily and another value may be more convenient.

The product of k consecutive convergents to Δx is

$$\prod_{r=n+1}^{r=n+k} \Delta_r x = (-1)^k \frac{U_n}{U_{n+k}} \tag{15}$$

The limit of this product as n increases without bound is $(\Delta x)^k$.

III. TREATMENT OF SPECIAL FORMS

In case $f(x) \equiv F(x^2)$, and x_0 is taken equal to zero, the derivatives of odd order are zero, and the functions U_{2m+1} are also zero. Thus, $\Delta_{2m} x = 0$ and $|\Delta_{2m+1} x| = \infty$. Taking n even and $k = 2$ in equation 15 gives

$$(\Delta_{2m+1} x)(\Delta_{2m+2} x) = \frac{U_{2m}}{U_{2m+2}} \tag{16}$$

This expression may be evaluated, giving a convergent to $(\Delta x)^2$. For instance, let $f(x) \equiv \cos x = 0$, and take $x_0 = 0$. Then U_{2m} becomes $\frac{E_m}{(2m)!}$, where E_m is Euler's number of order m, or Bernoulli's number of order $2m$, and

$$(\Delta_{2m+1} x)(\Delta_{2m+2} x) = \frac{(2m+1)(2m+2) E_m}{E_{m+1}} \tag{17}$$

Now $\lim_{m\to\infty}(\Delta_{2m+1}x)(\Delta_{2m+2}x)=(\Delta x)^2$ and $\lim_{m\to\infty}\frac{(2m+1)(2m+2)E_m}{E_{m+1}}=\frac{\pi^2}{4}$, so that $(\Delta x)^2=\frac{\pi^2}{4}$ or $\Delta x=\pm\frac{\pi}{2}$, which gives the roots $\pm\frac{\pi}{2}$ for $\cos x=0$.

The case in which $f(x)\equiv F[(x-c)^p]$ and $x_0=c$ may be treated in a different way. Put $(x-c)^p\equiv z$, and find Δz for $z_0=0$. Then $\Delta x=(\Delta z)^{1/p}$.

IV. APPLICATION OF RESULTS

The familiar equation $x^3-2x-5=0$ does not afford a good test of the method of this paper. If x_0 is taken as 2, the values of α_1, α_2, and α_3 are -10, -6, and -1. Thus, the successive values of U_n are integers, and may be written down immediately as far as U_4, which is sufficient for the calculation of the root correct to six decimal places.

The advantages of the method are better illustrated by the solution of a transcendental equation, such as

$$f(x)\equiv x+\sin x+\log x+e^x-5=0 \tag{18}$$

Taking $x_0=1.1$, we find

$a_0=$ 0.090 683 6
$a_1=$ 5.366 853
$a_2=$ 1.286 51 $\quad a_2/2 =$ 0.643 26
$a_3=$ 4.053 $\quad a_3/6 =$ 0.675 5
$a_4=-0.2 \quad a_4/24=-0.01$

TABLE 1.—*Table of the products necessary for the calculation of* $\Delta_4 x$.

	$\alpha_0=1$	$\alpha_1=\frac{a_1}{a_0}$	$\alpha_2=\frac{a_2}{2a_0}$	$\alpha_3=\frac{a_3}{6a_0}$	$\alpha_4=\frac{a_4}{24a_0}$
U_0	1	59. 182 18	7. 093 4	7. 449	−0. 1
U_1	59. 182 18	3, 502. 530	419. 80	440. 8	
U_2	3, 495. 437	206, 867. 6	24, 794		
U_3	206, 455. 2	12, 218, 46$_9$			
U_4	12, 194, 11$_8$				

$U_0=1$
$U_1=\alpha_1 \quad \Delta_1 x=-\ 1/U_1=-0.016\ 90$
$U_2=\alpha_1 U_1-\alpha_2 \quad \Delta_2 x=-U_1/U_2=-0.016\ 931\ 3$
$U_3=\alpha_1 U_2-\alpha_2 U_1+\alpha_3 \quad \Delta_3 x=-U_2/U_3=-0.016\ 930\ 7$
$U_4=\alpha_1 U_3-\alpha_2 U_2+\alpha_3 U_1-\alpha_4 \quad \Delta_4 x=-U_3/U_4=-0.016\ 930\ 7$

It may be seen that the value of α_4 was not significant in the calculation of U_4. The accuracy of the calculation is not increased by the last step, as $\Delta_3 x$ contains no error which is significant with respect to the value of a_0 used. Then $x_3=x_4=1.083\ 069\ 3$. The value of the root correct to eight decimal places is 1.083 069 29.

It should be noted that in solving equation 6 for Δx, $\varphi_n'(x_0)$ was used as a divisor. Thus, if $\varphi_n'(x_0)$ is zero or infinity, as may be the

case for certain values of x_0 and n, equation 7 does not hold. Generally this difficulty may be avoided by taking a higher value of n. $\varphi'_n(x_0)$ will not ordinarily be zero, however, if x_0 is a good approximation to a root.

As the derivation of equations 13 and 14 does not involve any assumptions other than that $f(x)$ is analytic, the equations hold for complex values of the coefficients or the roots. In the evaluation of complex roots of real equations it is convenient to use a complex value for x_0, as equation 15 must be used if x_0 is real. This treatment is not satisfactory, as the sequence U_n/U_{n+1} does not usually converge rapidly in such a case, and also because extraneous roots may be introduced.

V. SUMMARY

An expression is derived giving the roots of equations which involve only functions which may be expressed as power series. The expression involves only the values of the function and its derivatives at a given value of the variable.

Methods are given for the treatment of certain special forms.

An example is given of the application of the method to the evaluation of real roots.

WASHINGTON, November 22, 1934.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP791

Part of Journal of Research of the National Bureau of Standards, Volume 14, May 1935

HEATS OF REACTION OF THE SYSTEM: RUBBER-SULPHUR

By Archibald T. McPherson and Norman Bekkedahl

ABSTRACT

Heats of reaction of rubber with sulphur to form vulcanized compounds having empirical formulas lying between C_5H_8 and C_5H_8S (0 to 32 weight percent of sulphur) were determined directly at 175° C in an isothermal calorimeter, which consisted essentially of an insulated copper block to which heat could be added with electrical energy or removed by adding cold steel balls. In a reaction experiment, the mixture of rubber and sulphur was placed in a cavity in the copper block and the temperature of the block was maintained constant by the addition or removal of measured quantities of heat energy until the reaction of vulcanization was complete. Differences in heat content between 25 and 175° C, $(H_{175}-H_{25})$, for unvulcanized mixtures and vulcanized compounds of rubber and sulphur, were determined in the same calorimeter by dropping the sample at 25° C into the calorimeter at 175° C. For vulcanized compounds of rubber and sulphur, empirical formula $C_5H_8S_x$,

$$(H_{175}-H_{25})=22.2+1.2\,x$$

kilojoules per gram-mole of C_5H_8 in the range from $x=0$ to $x=0.5$, and

$$(H_{175}-H_{25})=24.1-2.6\,x$$

in the range from $x=0.5$ to $x=1.0$, where x is the number of atoms of sulphur per C_5H_8 and varies from 0 to 1.0. For unvulcanized mixtures of rubber and sulphur (C_5H_8+x S),

$$(H_{175}-H_{25})=22.2+6.2\,x$$

kilojoules per gram-mole of C_5H_8. The heat of the reaction of rubber with sulphur, which for the sake of simplicity may be represented as C_5H_8 (solid) $+x$ S (solid) $=C_5H_8S_x$ (solid), was found to be linear with x from $x=0$ to $x=0.5$, at which point there is a discontinuity in the slope of the curve; and also linear with a different slope for the range $x=0.5$ to $x=1.0$. In the composition range $x=0$ to $x=0.5$, the increases in heat content for the reaction of vulcanization at 175° and 25° C are respectively,

$$\Delta H_{175}=-60.0\,x, \text{ and}$$

$$\Delta H_{25}=-55.4\,x,$$

kilojoules per gram-mole of C_5H_8. In the range $x=0.5$ to $x=1.0$,

$$\Delta H_{175}=-22.5-15.0\,x, \text{ and}$$

$$\Delta H_{25}=-24.8-5.8\,x,$$

kilojoules per gram-mole of C_5H_8.

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1. Differences in heat content between 25 and 175° C	607
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I. INTRODUCTION

Previous investigators have employed two methods for determining the heat effects when rubber is vulcanized. In one method the heats of vulcanization are found by subtracting the heats of combustion of vulcanized rubber-sulphur compounds from the heats of combustion of the corresponding mixtures of rubber and sulphur before vulcanization.[1] This method is limited in precision by reason of the fact that the differences thus obtained are at most only a few percent of the measured heats of combustion. The other method, which has been used previously, involves the determination of the temperature rise which occurs when mixtures of rubber and sulphur are vulcanized. This method has, for the most part, been used for relative measurements, but Blake [2] has recently employed it for quantitative determinations of the heats of reaction of rubber with proportions of sulphur up to about 8 percent by weight. Recently Daynes [3] has employed a similar method for measurements over a wider range of composition.

This investigation was undertaken for the purpose of measuring the heats of reaction of rubber with different percentages of sulphur over the entire range of composition in which combination takes place. The study was exploratory in character, the aim being to make the measurements by direct means, with emphasis on simplicity rather than refinement of calorimetric procedure.

II. DESCRIPTION OF CALORIMETER

The calorimeter in which the reaction of rubber and sulphur was conducted consisted essentially of an insulated copper cylinder which served as a constant-temperature bath. This cylinder was 2¼ inches in diameter and 9½ inches long, and in it 4 holes were bored, ¼, ⅝, ⅝, and 1 inch, respectively, in diameter, and 9 inches in depth. As shown in figure 1, the cylinder was mounted in a 1-liter dewar flask, which was surrounded by thermal insulation and placed in a double-walled container. This container was maintained at constant temperature, about 175° C, by means of vapors of boiling cymene.

The temperature of the calorimeter was indicated by a mercury-in-glass thermometer, which was placed in the smallest hole, designated as K in the figure. The thermometer was graduated to 0.1° C and

[1] Jessup and Cummings, BS J.Research **13**, 357 (1934) RP713. Blake, Ind.Eng.Chem. **22**, 737 (1930). Hada, Fukaya, and Nakajima, J. Rubber Soc. Japan **2**, 389–397 (1931); Rubber Chem. Tech. **4**, 507 (1931).
[2] Ind. Eng. Chem. **26**, 1283 (1934).
[3] H. A. Daynes, paper presented at meeting of Institution of the Rubber Industry, Dec. 10, 1934.

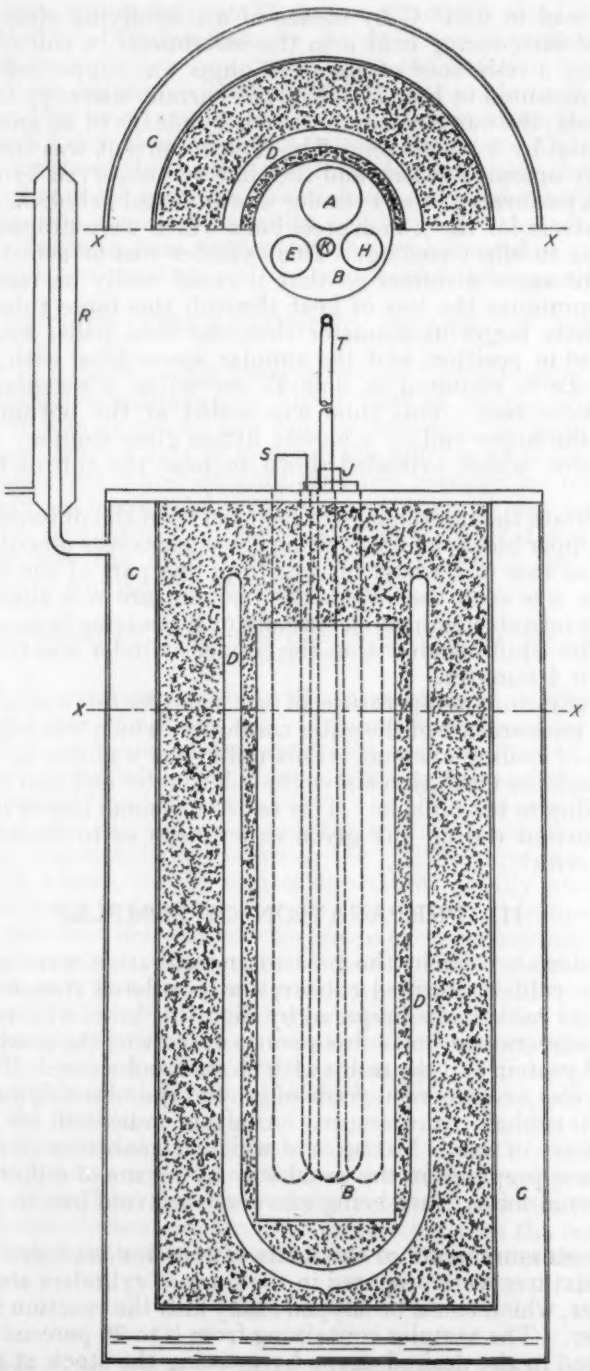

FIGURE 1.—*Cross section of the calorimeter used for the determination of the heats of reaction.*

A, cavity for the container of the steel balls; B, copper cylinder; C, cymene vapor bath; D, dewar flask; E, cavity for the sample tube; H, cavity for the calorimeter heater; J, tube leading to the container for the steel balls; K, cavity for the thermometer; R, reflux for the cymene vapors; S, sample tube; T, mercury thermometer.

could be read to 0.01° C by means of a magnifying glass. For the purpose of introducing heat into the calorimeter, a coil of nichrome wire having a resistance of about 40 ohms was supported on a glass tube and mounted in hole H. Electric current was supplied through copper leads; the current was measured by means of an ammeter, and the potential by a voltmeter. The flow of current was controlled by a manually operated switch and the time was observed by means of a watch. A perforated brass cylinder was mounted in hole A, and served as a receptacle for the ¼-inch steel balls which were dropped into the calorimeter to effect cooling. This cylinder was attached to a glass tube of the same diameter so that it could easily be removed. In order to minimize the loss of heat through this large tube a smaller tube, slightly larger in diameter than the steel balls, was mounted in it, sealed in position, and the annular space filled with insulation. A glass tube S, mounted in hole E, served as a receptacle for the sample under test. This tube was sealed at the bottom and was closed at the upper end by a loosely fitting glass stopper, not shown in the figure, which extended down to near the top of the copper cylinder.

To facilitate the interchange of heat between the different elements and the copper block, a high-melting ceresin wax was placed in all four holes. The rate of transfer of heat from one part of the calorimeter to another was such that when the temperature was changed a few degrees by introducing heat electrically or by putting in a cold sample, temperature equilibrium within the copper cylinder was reestablished within 3 or 4 minutes.

The equilibrium temperature of the calorimeter was about 1° C below the temperature of the outer container, which was kept constant by means of boiling cymene. This difference was due to the loss of heat through the insulation above the calorimeter and also through the tubes leading to the outside. This relatively small loss of heat was so nearly constant during any given experiment as to occasion no appreciable error.

III. PREPARATION OF SAMPLES

The materials used in the present investigation were commercial pale crepe rubber, purified rubber, and powdered rhombic sulphur. The purified rubber was prepared by digesting latex with steam at an elevated temperature, and subsequently extracting the products of hydrolysis of protein and the resins with alcohol and water.[4] The sulphur employed was a commercial grade of ground rhombic sulphur intended for use in rubber manufacture. Analysis indicated no impurities except a trace of ash. Mixtures of weighed quantities of rubber and sulphur were prepared in the usual way by means of either a roll mill or an internal mixer, care being exercised to avoid loss in the mixing process.

For the measurements of the heats of reaction, samples of rubber-sulphur mixtures were prepared in the form of cylinders about 10 mm in diameter, which could be slipped easily into the reaction tube of the calorimeter. The samples containing from 0 to 20 percent of sulphur were formed in the desired shape by pressing the stock at about 100° C in a rod mold lined with aluminum foil to prevent sticking. Samples

[4] BS J. Research 8, 751 (1932) RP449.

of stocks containing more than 20 percent of sulphur could not be used as solid cylinders of 10 mm diameter, because local superheating along the axis of the cylinders occurred during the reaction between the rubber and the sulphur. These samples were made in the form of hollow cylinders by wrapping the rubber stock in sheet form around weighed glass tubes of about 4 mm outside diameter. Correction for the heat capacity of these tubes was made in computing the results.

The samples which were vulcanized in the course of determining the heats of reaction were subsequently employed for the measurement of the differences in heat content of the rubber-sulphur compounds between room temperature and the temperature of the calorimeter.

IV. METHOD OF DETERMINING HEATS OF REACTION

In order to determine the heats of reaction of rubber and sulphur at the vulcanizing temperature, about 175° C, by the method here employed, it was necessary not only to measure the heat effects at that temperature but also to measure the differences in heat content of the *unvulcanized* rubber-sulphur mixtures between the temperature of the room, approximately 25° C, and that of the calorimeter. Furthermore, to obtain the heats of reaction at 25° C it was necessary to measure also the differences in heat content of the *vulcanized* rubber-sulphur compounds between 175 and 25° C.

1. MEASUREMENT OF DIFFERENCES IN HEAT CONTENT BETWEEN 25 AND 175° C

The experimental procedure in the measurement of differences in heat content was the following. Cymene was placed in the outer double-walled container of the apparatus and was heated to boiling by an electric hot plate. The copper cylinder was heated electrically to approximately the same temperature as the vapors of the boiling cymene and was allowed to stand for several hours until thermal equilibrium was established between the cylinder and the container. A sample of known weight and temperature, usually about 25° C, was slipped quickly into the sample tube of the calorimeter. The rubber samples were first dusted with talc to prevent their sticking to the sides of the glass tube. The weight of the talc used was not significant. Experiments in which the sample tube was opened and closed in the same manner without introducing a sample indicated that no significant quantity of heat was lost from the calorimeter in this operation. Heat was then added electrically to the copper cylinder in quantity sufficient to balance the heat taken up by the cold sample and bring it again to the previous equilibrium temperature. During this process the temperature variation was seldom greater than 1° C and the time of disturbance never over 4 minutes, so the results were probably not materially affected by the onset of the vulcanization reaction.

The difference in heat content of a sample between the temperature of the room and that of the calorimeter was found from the equation,

$$(H_c - H_r) = \frac{EIs}{m}$$

where H_c and H_r are the heat contents in joules per gram of the samples at the temperature of the calorimeter and of the room, respectively, s is the time of heating in seconds, E the potential in volts, I the current

in amperes, and m the weight of the sample in grams. Since the temperatures of the calorimeter and of the room are relatively close to 175° and 25° C, respectively, the difference in heat content between these temperatures, $(H_{175}-H_{25})$, can be computed from (H_c-H_r) without appreciable error.

2. MEASUREMENT OF HEATS OF REACTION

In determining the heat of reaction of a mixture of rubber and sulphur, a cylindrical sample was dusted with talc and dropped into the sample tube of the calorimeter. The quantity of heat required to restore the calorimeter to the equilibrium temperature was computed and was added electrically. With this heat added the calorimeter was ready for the measurement of the heat of reaction of the sample at the calorimeter temperature. Vulcanization proceeded with the liberation of heat. In order to determine this quantity of heat, steel balls at the temperature of the room were dropped into the calorimeter at such a rate as to keep the temperature constant. Since the balls were uniform in weight to within 0.1 percent it was only necessary to count them to obtain the mass of the metal added. The reaction, in all cases, was complete in about an hour, though observations of the temperature were made for at least one-half hour longer to insure that equilibrium had been reached.

The heat of reaction at the temperature of the calorimeter, in joules per gram of mixture, is given by the relation

$$\Delta H_{175}=\frac{-1.045N(0.510)(t_c-t_r)}{m}$$

where N is the number of steel balls added, 1.045 the weight in grams of each ball, m the weight in grams of the sample, and 0.510 the mean heat capacity in joules per gram per degree centigrade of the steel from 25 to 175° C, which were approximately the temperatures of the room and of the calorimeter, t_r and t_c, respectively.

The heat of reaction at 25° C was calculated from the equation

$$\Delta H_{25}=\Delta H_{175}+(H_{175}-H_{25})_{\text{unvulcanized}}-(H_{175}-H_{25})_{\text{vulcanized}}$$

where the last two terms represent differences in heat content between the temperatures indicated.

3. ILLUSTRATIVE EXPERIMENT

The data and results which were obtained in a typical experiment involving the measurement of heat of reaction and the differences in heat content between room temperature and vulcanizing temperature, of the reactant mixture and the product of reaction, are given in table 1.

TABLE 1.—*Calculation of the heat of reaction of a sample of rubber-sulphur mixture*

State of sample	Unvulcanized	Vulcanized
Composition of sample:		
Rubber, percent by weight	75.0	75.0
Sulphur, percent by weight	25.0	25.0
Sulphur, atoms per C_5H_8[a]	0.708	0.708
Weight of sample in grams	8.46	7.87
Gram-mole of C_5H_8 in sample	0.0933	0.0868
Temperature of calorimeter, ° C	176.2	178.2
Temperature of room, ° C	24.0	24.3
Determination of $(H_{175}-H_{25})$:		
Current, amperes	0.775	0.770
Potential, volts	30.8	30.9
Time, seconds	105.	85.
Quantity of heat added, joules	2,506.	2,022.
(H_e-H_r), j/g of sample	296.	257.
$(H_{175}-H_{25})$, j/g of sample	292.	250.
$(H_{175}-H_{25})$, j/gram-mole of C_5H_8	26,500.	22,700.
Determination of heat of reaction at 175° C:		
Steel balls added, number	38	
Steel added, weight in grams	39.7	
Mean heat capacity of steel, j/g/° C	0.510	
Total heat liberated by reaction, joules	3,081.	
$-\Delta H_{175}$ in j/g of sample	364.	
$-\Delta H_{175}$ in j/gram-mole of C_5H_8	33,000.	
Determination of heat of reaction at 25° C:		
$(H_{175}-H_{25})_{\text{unvulc.}}-(H_{175}-H_{25})_{\text{vulc.}}$ in j/gram-mole of C_5H_8	3,800.	
$-\Delta H_{25}$ in j/gram-mole of C_5H_8	29,200.	
$-\Delta H_{25}$ in j/g of sample	322.	

[a] The computation of atoms of sulphur per C_5H_8 was made as if the rubber were all C_5H_8.

V. RESULTS OF CALORIMETRIC DETERMINATIONS

1. DIFFERENCES IN HEAT CONTENT BETWEEN 25 AND 175° C

The differences in heat content between 25 and 175° C for the various samples are given in table 2. The average value of $(H_{175}-H_{25})$ for the rubber alone is 326 joules per gram, which is equivalent to a mean heat capacity of 2.17 joules per gram per degree centigrade over this range. This value is of the same order or magnitude as other

TABLE 2.—*Differences in heat content between 25 and 175° C of rubber, sulphur, rubber-sulphur mixtures, and rubber-sulphur compounds*

Composition of sample				Difference in heat content $(H_{175}-H_{25})$	
Rubber		Sulphur			
Condition	Amount	Amount	Atoms per C_5H_8[a]		
	Percent	*Percent*		(j/g)	
Purified	100	0	0	331	
Do	100	0	0	321	
Do	0	100		191	
Do	0	100		196	
				Mixture	Compound
Purified	95.5	4.5	0.100	318	
Crude	95.5	4.5	.100		309
Purified	91.0	9.0	.210	314	
Crude	91.0	9.0	.210		304
Purified	82.0	18.0	.467	301	
Crude	82.0	18.0	.467		273
Do	78.0	22.0	.599	296	
Do	75.0	25.0	.708	301	
Do	75.0	25.0	.708	292	
Do	75.0	25.0	.708		250
Do	75.0	25.0	.708		240
Do	75.0	25.0	.708		250
Purified	68.0	32.0	1.00	278	
Crude	68.0	32.0	1.00		220
Do	68.0	32.0	1.00		217
Do	68.0	32.0	1.00		212

[a] The computation of atoms of sulphur per C_5H_8 was made as if the rubber were all C_5H_8.

determinations reported in the literature,[5] the more reliable of which lie between 2.0 and 2.2 joules per gram per degree centigrade. Strict comparison cannot be made between these different values since they relate to different temperature ranges. The difference in heat content for sulphur between 25 and 175° C was found to be 194 joules per gram. Calculations from data given in the literature [6] for the heat capacities of solid and liquid sulphur and the heat of fusion give a value of 191 joules per gram for this difference.

The differences in heat content between 25 and 175° C of both unvulcanized rubber-sulphur mixtures and vulcanized rubber-sulphur compounds are shown in figure 2 as functions of the sulphur content in percentage by weight. For the unvulcanized mixtures a straight line was drawn between the values at 0 and 100 percent of sulphur. This involves the assumption that the heat content of the mixture follows a simple additive relation and leaves out of consideration the heat of solution of rubber in sulphur and the interfacial energy between the rubber and the sulphur, both of which are probably very small.

Evidence of the linear relation between the differences in heat content of rubber-sulphur mixtures and the composition of such mixtures in percentage of sulphur by weight was obtained by observing the quantity of heat required to bring the calorimeter to the equilibrium temperature after a sample of mixture at room temperature had been added. This was not a precise determination because the liberation of heat by the vulcanization reaction became appreciable in a very few minutes, but, as shown in the figure, the observations are in fair agreement with the linear relation. The values for the rubber-sulphur compounds, also shown in figure 2, cannot be adequately represented by a single linear equation. However, two linear equations intersecting at the composition 19 percent of sulphur (0.5 atom of sulphur per C_5H_8) fit the results fairly well. This method of representation was chosen since it is shown later in this paper that the heats of reaction indicate the formation of compounds above 19 percent of sulphur dissimilar to those formed at lower percentages of sulphur. It would be expected that a break in the heat-content curve would most probably occur at this point, and the curve was drawn accordingly. The shape of the curve, however, does not materially affect the values obtained for the heats of vulcanization.

Equations were derived from the curves drawn in figure 2 expressing the differences in heat content in kilojoules per gram-mole of C_5H_8 for compositions in terms of molecular ratios.[7] For the unvulcanized mixtures,

$$(H_{175}-H_{25})=22.2+6.2x$$

kilojoules per gram-mole of C_5H_8, where x represents the number of sulphur atoms per C_5H_8. This equation holds true for all values of x. For the vulcanized rubber-sulphur compounds

$$(H_{175}-H_{25})=22.2+1.2x$$

[5] See Gee and Terry, Brit. Assoc. Advancement Sci. page 516 (1889); Mem. Proc. Manchester Lit. Phil. Soc. [4] **4**, 38 (1890–1891); Ruhemann and Simon, Z. physik. Chem. [A] **138**, 1 (1928); LeBlanc and Kröger, Z. Elektrochemie **34**, 241 (1928); and Boström, Kolloidchem. Beihefte **26**, 439 (1928).

[6] Lewis and Randall, J. Am. Chem. Soc. **33**, 476 (1911); Lewis and Randall, Thermodynamics. (McGraw-Hill Book Co., New York, 1923); and Monval, Bul. soc. chim. [4] **39**, 1349 (1926).

[7] It may be well to note that if the curves for the heat of reaction or heat content per gram of mixture are linear with the weight percent of sulphur, then the corresponding curves per mole of C_5H_8 are linear with the number of atoms of S per C_5H_8.

kilojoules per gram-mole of C_5H_8, from $x=0$ to $x=0.5$. From $x=0.5$ to $x=1.0$

$$(H_{175}-H_{25})=24.1-2.6x$$

kilojoules per gram-mole of C_5H_8. The observations agree with the values indicated by these equations with a maximum deviation of 0.6 and an average deviation of 0.2 kilojoule per gram-atom of C_5H_8.

The mean heat capacity between 25 and 175° C was determined for the steel balls used to absorb heat from the calorimeter in the measurements of the heats of the reaction. The average value obtained was 0.510 joule per gram per degree centigrade. Levin and Schottky [8] give data from which a value of 0.507 was computed for steel of 1 percent carbon content in the range of temperature covered by this investigation. The steel balls had approximately the same carbon content. The mean heat capacity of the glass used as a core for some

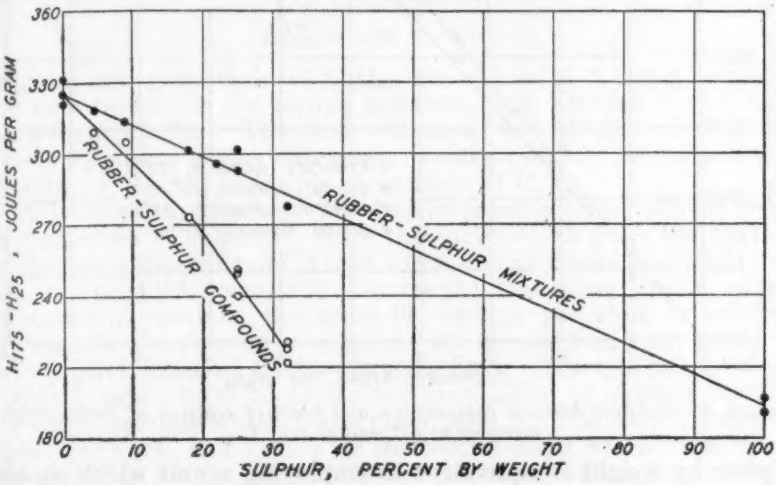

FIGURE 2.—*Relation between composition and differences in heat content between 25 and 175° C of rubber-sulphur compounds and mixtures*

of the rubber samples was also determined and was found to be 0.85 joule per gram per degree centigrade, which is in practical agreement with the value of 0.84 given in the literature for laboratory pyrex glass.[9] Since the calorimeter was operated isothermally its heat capacity was not required for the computation of the results. It was of interest, however, in connection with the precision of the method since this is dependent on the amount by which the temperature of the calorimeter is changed by the addition or removal of a given quantity of heat. The heat capacity was of the order of 2,300 joules per degree centigrade. This means that when a steel ball at 25° C was dropped into the calorimeter at 175° C the temperature was lowered by about 0.033° C.

2. HEATS OF REACTION AT 175° AND 25° C

The heats of reaction of different mixtures of rubber and sulphur at 175° and 25° C are given in table 3. The same results are shown graphically in figure 3, the heats of reaction in joules per gram-mole

[8] Ferrum **10**, 193 (1913).
[9] International Critical Tables, **2**, 93 (1927) (McGraw-Hill Book Co., New York, N. Y.)

of C_5H_8 being plotted against the number of atoms of sulphur per C_5H_8. This method of expressing the results was adopted because it provides as a basic unit a fixed chemical quantity, C_5H_8. The convention followed by previous investigators of plotting the heats of reaction per gram of mixture against the composition in percentage of

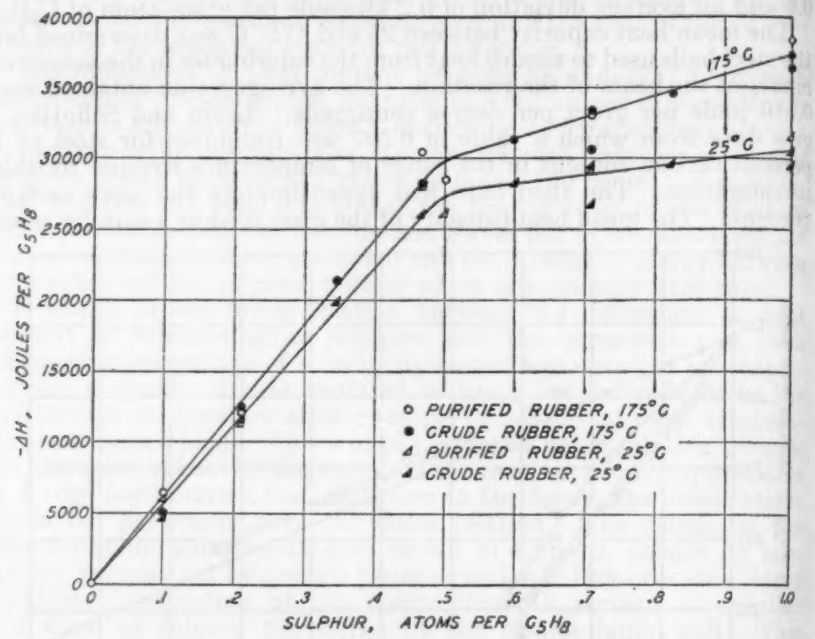

FIGURE 3.—*Relation between composition and heats of reaction of rubber-sulphur mixtures at 25° and at 175° C.*

sulphur by weight is equivalent to employing a unit which changes with composition.

TABLE 3.—*Heats of reaction of rubber-sulphur mixtures.*

Composition of sample				Heats of reaction ($-\Delta H$)	
Rubber		Sulphur			
Condition	Amount	Amount	Atoms per C_5H_8*	At 175° C	At 25° C
	Percent	*Percent*		*Kilojoules/gram-mole of* C_5H_8	
Purified	95.5	4.5	0.100	6.4	5.9
Crude	95.5	4.5	.100	5.0	4.5
Purified	91.0	9.0	.210	12.1	11.1
Crude	91.0	9.0	.210	12.4	11.4
Do	86.0	14.0	.346	21.3	19.6
Purified	82.0	18.0	.467	30.4	28.1
Crude	82.0	18.0	.467	28.2	25.9
Purified	81.0	19.0	.499	28.5	26.0
Crude	78.0	22.0	.599	31.3	27.9
Purified	75.0	25.0	.708	33.0	28.7
Crude	75.0	25.0	.708	30.7	26.4
Do	75.0	25.0	.708	33.4	29.1
Do	72.0	28.0	.826	34.6	29.3
Purified	68.0	32.0	1.00	38.4	31.6
Crude	68.0	32.0	1.00	36.4	29.5
Do	68.0	32.0	1.00	37.4	30.5

* The computation of atoms of sulphur per C_5H_8 was made as if the rubber were all C_5H_8.

The results plotted in figure 3 may be represented within experimental error by straight lines of different slopes. Discontinuity in the slope occurs for each curve at a composition corresponding to 0.5 atom of sulphur per C_5H_8. The two portions of the curve representing the heats of reaction at 175° C are described by the following equations:

$$\Delta H_{175} = -60.0\ x$$

kilojoules per gram-mole of C_5H_8, from $x=0$ to $x=0.5$ atom of sulphur per C_5H_8, and

$$\Delta H_{175} = -22.5 - 15.0\ x,$$

from $x=0.5$ to $x=1.0$. Similarly the two portions of the curve for the heats of reaction at 25° C are described by the equations:

$$\Delta H_{25} = -55.4\ x, \text{ and}$$

$$\Delta H_{25} = -24.8 - 5.8\ x$$

kilojoules per gram-mole of C_5H_8, the values of x lying between $x=0$ and $x=0.5$ for the former equation, and between $x=0.5$ and $x=1.0$ for the latter. The observations agree with the values given in these equations with a maximum deviation of 2.3, and an average deviation of 0.6, kilojoules per gram-mole of C_5H_8.

The heats of reaction may also be expressed in terms of heat units per gram-atom of sulphur. Since the curve which gives the heat of reaction per gram-mole of C_5H_8 as a function of the number of atoms of sulphur per C_5H_8 consists of two straight lines corresponding to the two stages of reaction, the heats of reaction per atom of sulphur entering into the respective reactions are constant and are equal to the respective slopes of the two straight lines. The numerical values at 175° C are −60.0 kilojoules per gram-atom of sulphur for the first stage reaction, which takes place from $x=0$ to $x=0.5$ atom of sulphur per C_5H_8, and −15.0 for the second stage, which takes place from $x=0.5$ to $x=1.0$. At 25° C the numerical values are $-55.4\ x$ and $-5.8\ x$ kilojoules per gram-atom of sulphur for the first and second stage reactions, respectively.

In calculating the composition of the samples in atoms of sulphur per C_5H_8, the rubber, whether crude or purified, was treated as if it were all rubber hydrocarbon. This procedure is warranted, in the present case, by the fact that there is no significant difference in the results for the two kinds of rubber, as shown in table 3 and figure 3. More precise measurements, however, would doubtless indicate a difference, since it is well known that not only the hydrocarbon but also the resins and proteins of crude rubber react with sulphur.

Some experiments were conducted in which rubber-sulphur compounds, vulcanized with less than the maximum amount of sulphur, were further vulcanized with additional sulphur. The quantity of heat liberated was in agreement with the value calculated by subtracting the heat of reaction of rubber with the initial percentage of sulphur from the heat of reaction with the final percentage as read from figure 3. In one such experiment vulcanized rubber containing 19 percent of sulphur ($C_5H_8S_{1/2}$) was ground and mixed with additional sulphur to correspond to a composition of 32 percent (C_5H_8S). Because of the bulk of the mixture the largest sample that could be used was less than half the ordinary size, and the precision was cor-

respondingly reduced. On vulcanization the heat liberated was 5.5 kilojoules per gram-mole of C_5H_8. Curve 3 indicates a value of about 30.0 kilojoules per gram-mole of C_5H_8 for the vulcanization of rubber with 19 percent of sulphur. The addition of 5.5 kilojoules to this gives a value of 35.5 kilojoules per gram-mole of C_5H_8, which may be compared with the value 37.5 which is indicated by the curve for the compound containing 32 percent of sulphur.

VI. COMPARISON WITH PREVIOUS INVESTIGATIONS

A comparison of the heats of reaction at 25° C, which are given in table 3, with the heats of reaction found in some previous investigations is shown in figure 4. In preparing this figure the convention of

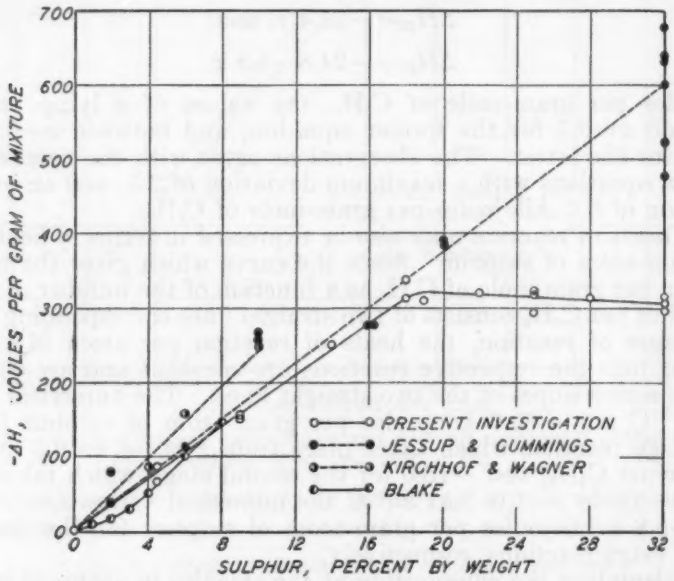

FIGURE 4.—*Relation between composition and heats of reaction of rubber-sulphur mixtures determined by various investigators.*

previous investigators has been followed in expressing the heats of reaction in joules per gram of mixture, and the composition in percentage of sulphur by weight.[10] The results of Kirchhof and Wagner [11] are somewhat higher than those of the present investigation and extend to only 10 percent of sulphur. These investigators were chiefly concerned with the effect of fillers and accelerators on the heats of vulcanization and reported only a few observations on mixtures of rubber and sulphur alone. The results of Blake [12] are lower than those of the present investigation and indicate that the heat of reaction is not a linear function in the range from 0 to 8 percent of sulphur.

[10] See footnote 7.
[11] Gummi-Zeitung **39**, 572 (1924–1925).
[12] Ind. Eng. Chem. **26**, 1283 (1934).

The results reported by Jessup and Cummings [13] agree well with the present results for the range from 0 to 19 percent of sulphur. Their curve exhibits no discontinuity in the slope at this point, hence their values for the compositions from 19 to 32 percent of sulphur are higher than the present values. This discrepancy at the higher percentages of sulphur may be due to differences in the conditions of vulcanization employed in the two investigations. The samples used by Jessup and Cummings were vulcanized for about 40 hours at 141° C in an autoclave containing inert gas under pressure, while in the present work the samples were vulcanized for about 1 hour at 175° C in a glass tube, one end of which was open to the air.

The results of an earlier investigation by Blake and of an investigation by Hada, Fukaya, and Nakajima [14] are considerably at variance with those here considered and are not shown in figure 4 because of the scale used.

A salient feature of this study is the change of slope obtained in the curve for the heat of vulcanization at the composition 0.5 atom of sulphur per C_5H_8 (19 percent of sulphur by weight). This is an indication that the reaction of rubber with sulphur takes place in two stages, the first liberating a greater quantity of heat than the second. The suggestion of a two-stage reaction between rubber and sulphur is by no means novel, a variety of evidence for it having been presented by different authors.[15] In some instances the evidence relates to changes in properties which are associated with the fortuitous circumstance that the transition between soft and hard rubber occurs at room temperature at the composition, 0.5 atom of sulphur per C_5H_8. This evidence is shown not to hold when the properties under consideration are measured at other temperatures and pressures. Other types of evidence, however, such as the reaction between vulcanized rubber and alcoholic potash described by Whitby and Jane,[16] seem to constitute valid evidence for a two-stage reaction. Definite conclusions, however, cannot be drawn until the mechanism of the reaction of rubber with sulphur is established.

WASHINGTON, December 20, 1934.

[13] BS J. Research **13**, 357 (1934) RP713.
[14] Blake, Ind. Eng. Chem. **22**, 737 (1930). Hada, Fukaya, and Nakajima, Rubber Chem. Tech. **4**, 507 (1931).
[15] Blake, Ind. Eng. Chem. **22**, 737 (1930); **26**, 1283 (1934); Hada, Fukaya, and Nakajima, Rubber Chem. Tech. **4**, 507 (1931); Williams and Beaver, Ind. Eng. Chem. **15**, 255 (1923); Glancey, Wright, and Oon, Ind. Eng. Chem. **18**, 73 (1926); and Davies, Trans. Inst. Rubber Ind. **10**, 176 (1934). Curtis, McPherson, and Scott, in BS Sci. Pap. **22**, 398 (1927) S560, suggested the existence of definite compounds of rubber and sulphur on the basis of changes in electrical properties and density with composition. It was later shown by Kimura, Aizawa, and Takeuchi, J. Inst. Elec. Engrs., Japan, no. 485, 1274 (December 1928), and Kitchin, J. Am. Inst. Elec. Engrs. **48**, 281 (1929), and Kimura and Namikawa, J. Soc. Chem. Ind., Japan, **32** (supplemental binding), 196B (1929) that the agreement between changes in electrical properties and the compositions represented by simple empirical formulas was fortuitous and without basic significance.
[16] Trans. Roy. Soc. Canada [3], **20**, 121 (1926).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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THERMAL BEHAVIOR OF THE KAOLIN MINERALS

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ABSTRACT

When minerals of the kaolin group are heated at constant rates there are two principal heat effects, a broad, pronounced endothermic effect near 550° C and a sharp, intense exothermic effect near 950° C. New evidence, based largely on X-ray patterns of the kaolin minerals and of artificial alumina-silica gels after various heat treatments, leads to the following conclusions: (1) The endothermic effect is due to the dissociation of the kaolin minerals into water vapor and an intimate mixture of amorphous Al_2O_3 and amorphous SiO_2; (2) The exothermic effect is caused by the crystallization of γ-Al_2O_3 from amorphous Al_2O_3; (3) The delay in the crystallization of γ-Al_2O_3 until higher temperatures are reached and the resultant intensity of the effect produced are due to the restraining action of the rigid amorphous SiO_2 network with which the Al_2O_3 is closely associated.

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I. INTRODUCTION

Since Le Chatelier's [1] discovery of the thermal effects obtained when clays are heated, there have been numerous investigations [2] to determine the cause of these effects, and at least three distinct theories have been developed. Much of the resulting confusion has been caused by: (1) The use of materials which contained large amounts of impurities or which were mixtures of different species of clay minerals; (2) Unfortunate selection of the experimental methods; (3) The assumption that samples heated at constant temperature for long periods of time contain the same phases as samples withdrawn from the furnace immediately at the attainment of that temperature.

A part of the confusion has been eliminated by the work of Ross and Kerr,[3] who discovered the existence of three minerals of the kaolin

[1] Z. Phys. Chem. 1, 396 (1887).

[2] A comprehensive review of the theories and the experimental work is given by K. Spangenberg, Keram. Rundschau 35, 331–335, 352–354, 370–372 (1927).

[3] The Kaolin Minerals, U. S. Geol. Survey Professional Papers 165-E (1930).

group, nacrite, dickite, and kaolinite, with the same chemical composition ($Al_2O_3.2SiO.2_2H_2O$) but with distinctive crystal structures.[4]

The purpose of the present work has been to determine more precisely the nature of the heat effects when clay minerals are heated at controlled rates and to discover the changes in structure and constituents which accompany these heat effects.

II. MATERIALS INVESTIGATED

Two kaolin minerals, dickite and kaolinite, were the natural materials on which most of the experiments reported here were made. The heat effects in various other clays were observed for comparison, but because of the lack of knowledge of their constitution and purity the results were inconclusive. The dickite, obtained through the courtesy of W. F. Foshag, of the U. S. National Museum, was from the National Belle Mine, Red Mountain, Colo. The material occurs as a loose powder, and with a low-power microscope it is found to be made up of individual crystals with perfect basal cleavage and hexagonal outline. The kaolinite chosen for these experiments was the washed Zettlitz kaolin distributed as an international standard by the Ceramic Society of Czechoslovakia. The optical and crystallographic properties of these two kaolin minerals are given by Ross and Kerr.[5] Chemical analyses are given in table 1.

TABLE 1.—*Chemical analyses of kaolin minerals*

Constituents	Zettlitz kaolin [a]	Red Mountain dickite [b]	Constituents	Zettlitz kaolin [a]	Red Mountain dickite [b]
	Percent	*Percent*		*Percent*	*Percent*
SiO_2	46.90	46.35	Cr_2O_3	.015	.....
Al_2O_3	37.40	39.59	V_2O_3	.002	.....
Fe_2O_3	.65	.11	K_2O	.84	.....
P_2O_5	.08	.....	Na_2O	.44	.....
TiO_2	.18	.....	SO_3	.03	.....
ZrO_2	.007	.....	F	.....	.15
MnO	.007	.....	F=O	.....	−0.06
CaO	.29	.....	Loss on ignition	12.95	13.93
MgO	.27	.....			
BaO	.02	.....	Totals	100.087	100.13
SrO	.006	.....			

[a] Analysis from BS Tech. News Bul. 138, p. 146 (1928).
[b] W. F. Hillebrand, analyst, U. S. Geol. Survey Bul. 20, p. 97 (1885).

Synthetic materials studied included five Al_2O_3–SiO_2 coprecipitated gels with approximate Al_2O_3:SiO_2 ratios of 1:4, 1:2, 1:1, 2:1, and 4:1, and four other mixed gels, gels A, B, C, and D, all with Al_2O_3:SiO_2 equal to 1:2. The coprecipitated gels were prepared as follows. An analyzed solution of sodium silicate (containing 68 g of SiO_2 per liter) was measured out and solid $Al_2(SO_4)_3.18H_2O$ was weighed out in proportions to give the desired molar ratio. The salt was dissolved in water (about 100 cc per 4 g of salt) and the silicate solution added dropwise with vigorous stirring. Then 10 percent NaOH solution was added to neutrality as shown by phenol red indicator. The voluminous, gelatinous precipitate was filtered, dried, ground to pass

[4] J. W. Gruner, Crystal structure of kaolinite. Z. Kryst. **83**, 75–88 (1933); Crystal structure of dickite. Z. Kryst. **83**, 394–404 (1932); Crystal structure of nacrite and a comparison of certain optical properties of the kaolin group with its structure. Z. Kryst. **85**, 345–354 (1933).
[5] The Kaolin Minerals, U. S. Geological Survey Professional Papers 165–E (1930).

a no. 200 sieve, washed thoroughly on a filter with hot water and redried at 110° C. Analysis of three of the 1:2 gel preparations gave Al_2O_3:SiO_2 ratios of 1:1.99, 1:1.90, and 1:1.88, respectively. A soda determination on the 1:1.88 product showed it to contain 0.65 percent of Na_2O. Therefore, another 1:2 gel was made, using aluminum chloride instead of aluminum sulphate, and the product was electrodialyzed for 10 hours in a Bradfield two-compartment electrodialysis cell to free it of sodium ions. Analysis after this treatment gave 0.09 percent of Na_2O. All these coprecipitated gels were found to consist of clear, angular, isotropic grains when examined under the microscope. X-ray photographs showed them to be amorphous. The Al_2O_3 in these gels was completely soluble in dilute HCl.

Other mixed gels were made as follows:

Gel A.—Al_2O_3 and SiO_2 gels were precipitated in separate vessels, allowed to settle, and, after decanting, mixed together with vigorous stirring. The combined precipitate was then filtered and the gel cake mashed thoroughly in a mortar. The product was ground and washed with hot water as described above.

Gel B.—Finely ground (through a no. 325 sieve) dried Al_2O_3 and dried SiO_2 gels were mixed in weighed proportions, moistened, and ground thoroughly in a mortar for two hours.

Gel C.—Fine (through a no. 325 sieve) particles of dried Al_2O_3 gel were suspended in water. Sodium silicate solution and dilute HCl solution were then added drop by drop simultaneously so that the solution was always kept neutral. Silica gel precipitated around each Al_2O_3 particle giving a voluminous flocculent precipitate.

Gel D.—Prepared the same as gel C except that the Al_2O_3 gel was first heated to 800° C for 24 hours, thereby converting it to γ-Al_2O_3.

III. EXPERIMENTAL METHODS

Thermal effects were measured by the Le Chatelier differential thermocouple method. A platinum-wire resistance furnace, a divided platinum cylinder, a Pt-Rh to Pt to Pt-Rh differential thermocouple, and a type K potentiometer were used. Artificial alpha-alumina, known to show no measurable heat effects, was used as a reference material. The furnace temperature was increased at a constant rate by manually decreasing the resistance in series with the furnace at regular time intervals. The normal heating rate selected was 6° C/min, but rates between 1 and 25° C per minute were also used. Readings of the temperature of the sample and of the galvanometer deflection due to the temperature difference between the two sides of the cylinder were made at intervals of 1 minute or less. These readings were plotted in the usual manner as shown in figures 1 and 4.

Determinations of the crystalline compounds present in the samples were made by comparison of X-ray powder diffraction patterns, using either a Coolidge type tube with Mo $K\alpha$ radiation and a camera of 20.8-cm radius, or an ion tube of the type developed by Ksanda [6] with Cu $K\alpha$ radiation and a camera of 4.1-cm radius. Cameras for both tubes were so arranged that comparison patterns of two materials could be photographed on the same film.

[6] Rev. Sci. Instr. **3**, 531-534 (1932).

Supplemental examinations were made with the petrographic microscope, but in most cases the materials were so fine grained that the results were not conclusive.

IV. DATA AND DISCUSSION

1. INTRODUCTORY

When samples of dickite or kaolinite are heated at an approximately constant rate of 6° C/min, three heat effects are observed (fig. 1), which in order of occurrence with increasing temperature are: (1) A large endothermic effect which occurs over a broad temperature range;

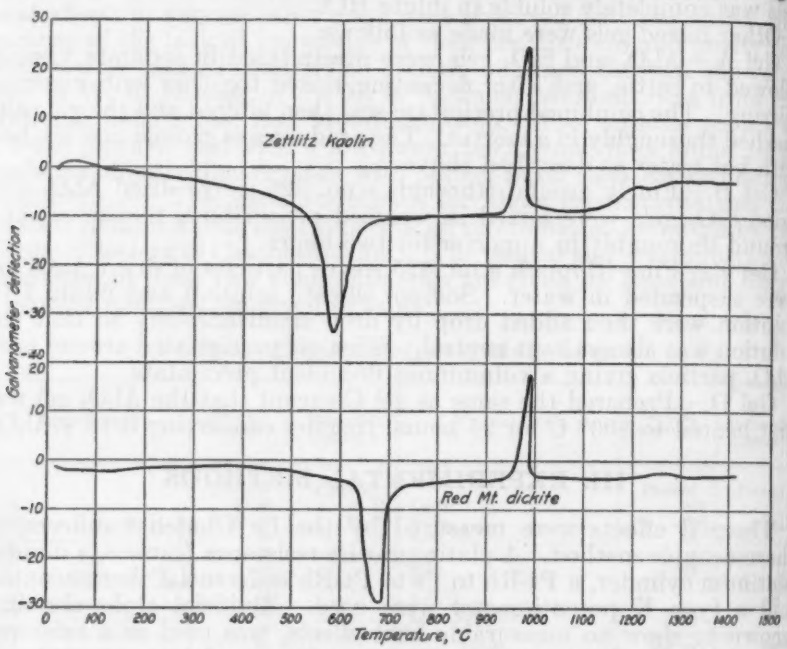

FIGURE 1.—*Heating curves of kaolinite and dickite.*

(2) a large exothermic effect which is very sharp and intense and occurs over a narrow temperature range; (3) a very small exothermic effect which occurs over a broad temperature range and which is frequently difficult to detect.

When a sample which has been heated to any temperature is cooled no heat effects are observed during the cooling; when the sample is reheated no heat effects are observed up to that temperature, but the heat effects above that temperature are unaffected. Therefore, all of the reactions causing these heat effects are irreversible.

This paper is concerned with the first two of these heat effects.[7]

[7] The third heat effect begins at about 1,150° C and ends at about 1,250° C. Since it is evidenced in X-ray patterns only by an intensification of the mullite lines, it probably represents the temperature range in which the formation of mullite takes place most rapidly.

2. THE ENDOTHERMIC HEAT EFFECT

The endothermic effect occurs over a wide temperature range from about 450 to about 580° C in Zettlitz kaolin and from about 550 to about 680° C [8] in Red Mountain dickite. This heat absorption is definitely related to the loss of "combined" water, as has been shown by Sokoloff,[9] Tammann and Pape,[10] Rhode,[11] van Nieuwenburg and Pieters,[12] and Nutting.[13] All of these investigators made determinations of weight losses at constant temperatures, and all of them obtained values in fair agreement for experiments carried out in contact with the room atmosphere. A few experiments on dickite and kaolinite made in this investigation also confirm these results. The results of all agree in showing that the dehydration takes place over a considerable temperature range and that with constantly increasing temperature there is no single temperature at which all the combined water can be expelled.

The most complete and decisive work on the dehydration temperature was done by van Nieuwenburg and Pieters who, using Zettlitz kaolin and Neurode pholerite (dickite), measured the vapor pressures for different temperatures and for different water contents. They conclude that: (1) The dissociation pressure is a function of the water content over the whole range of dissociation; (2) The *p-t-x* diagram is not a true equilibrium diagram because, in part, of the very small particle size of ordinary kaolin.

Their conclusion that the water loss of Neurode pholerite at significantly higher temperatures than that of Zettlitz kaolin is due to the coarser grain of the former, is open to some doubt because of the discovery by Ross and Kerr [14] that Neurode pholerite (dickite) has a different crystalline structure from Zettlitz kaolin (kaolinite). That the dickite investigated does lose its water at higher temperatures than the kaolinite available for study is shown also by the heating curves of figure 1 and by the weight-loss temperature experiments of Nutting.[15] The final solution of this part of the problem awaits a supply of pure kaolinite of uniform coarse grain for measurements of dehydration temperatures under controlled water-vapor pressures.

The knowledge available on the dehydration relations of the dissociation process assists very little in answering the question as to the nature of the dissociation process. To determine the nature of the products, samples of kaolinite and dickite were heated at 6° C/min to temperatures at which the original X-ray pattern had completely disappeared, namely, from 700° C up to the beginning of the exothermic effect (about 925° C). Samples air-quenched from temperatures in this range gave no X-ray patterns attributable to crystalline materials; the patterns all consisted of a broad, diffuse band characteristic of amorphous materials.

[8] These values represent, respectively, the beginning of rapid absorption of heat and the temperature at which the absorption is complete (minimum on the differential heating curve) for the particular experimental conditions. Different experimental conditions, especially different heating rates, will change these values somewhat. The temperature representing the beginning of rapid absorption of heat is indefinitely located on the curve and hence difficult of reproduction. The temperature at which the absorption is complete is definitely located on the curve and can be reproduced to within ±3° C with the same material, apparatus, and heating rate.

[9] Tonind. Z. **36**, 1107–1110 (1912).

[10] Z. anorg. allgem. Chem. **127**, 43–68 (1923).

[11] Keram. Rundschau **35**, 398–401, 414–415, 434–435, 452–454, 470–471 (1927).

[12] Rec. trav. Chim. **48**, 406–416 (1929).

[13] The Bleaching Clays. U. S. Geol. Survey Cir. 3 (1933).

[14] The Kaolin Minerals. U. S. Geol. Survey Professional Papers 165–E (1930).

[15] The Bleaching Clays. U. S. Geol. Survey Cir. 3 (1933).

The only direct evidence that a crystalline material results from the dehydration of kaolin is that of Hyslop and Rooksby,[16] who found that samples of English china clay when heated to temperatures between 650° and 850° C gave a diffraction pattern of a crystalline material, which they called "alpha" and which they assumed to be a crystalline anhydrous alumino-silicate, probably $Al_2O_3.2SiO_2$. English china clay is known to be a somewhat impure kaolin, and petrographic examinations[17] have shown that a sample of washed English china clay contained about 10 percent of muscovite mica. A sample of this clay in one compartment of a divided crucible with muscovite mica in the other compartment was heated to 750° C at 12° C/min and air-quenched. The sample afforded a faint X-ray diffraction pattern, five lines of which could be readily distinguished and measured. These lines were identical in position with the five strongest lines of the pattern of the muscovite mica heated simultaneously and their calculated positions agreed well with those given by Hyslop and Rooksby in a diagram of the "alpha" pattern.

Since dehydrated kaolin is amorphous, and not crystalline, the question arises as to whether it is: (1) An intimate mixture of amorphous alumina and amorphous silica; (2) An amorphous compound of alumina and silica (anhydro-kaolin or meta-kaolin).

Both of these hypotheses have been advanced in the literature.[18] In section IV–3 (b) evidence will be advanced in support of the first hypothesis.

The only evidence of any phase changes between the temperatures of the endothermic and exothermic heat effects is that given by Schwarz and Klos.[19] They postulate a phase change at 870° C based solely on very small inflections in the thermal-expansion curve of clays. Such inflections do not necessarily represent changes in phase. The most sensitive methods of detecting thermal effects which have been used on the clay minerals, those of Houldsworth and Cobb[20] and ourselves, fail to show any effects at or near 870° C.

3. THE EXOTHERMIC HEAT EFFECT

(a) EXPERIMENTAL RESULTS

The exothermic effect is a rapid evolution of heat beginning at about 925° C and, with a heating rate of 6° C/min, reaching a maximum at 985° C.[21] Under the conditions of the present experiments the increase of temperature of the sample over that of the reference material may be as much as 30° C. The characteristics of the effect, including temperature and intensity, are identical for kaolinite and dickite. For heating rates between 1 and 20° C/min the temperature of the beginning of heat evolution does not vary more than 4° C, but because of the rate at which the heat is evolved, the temperatures of the maximum may be widely different, ranging from 957° C for a heating rate of 1° C/min to 1,013° C for a heating rate of 20° C/min.

[16] Trans. Ceram. Soc. **27**, 93–96 (1927–1928).
[17] R. H. Ewell, BS J. Research **8**, 202 (1932) RP 410.
[18] Mellor and Holdcroft, Trans. Ceram. Soc. **10**, 94 (1911), first advanced the hypothesis of the decomposition into alumina, silica and water on the evidence of similarities in the properties of amorphous alumina and dehydrated kaolinite.
[19] Z. anorg. Chem. **196**, 213–219 (1931).
[20] Trans. Ceram. Soc. **22**, 111–137 (1922–23).
[21] See footnote 8, p. 619. The reproducibility in this case is ± 4° C for the lower temperature and ± 2° C or the upper temperature, with the same material, apparatus, and heating rate.

In order to show the changes in phase which accompany the exothermic effect, samples of kaolinite and dickite were heated at 6° C/min to temperatures just below the beginning of the effect (925° C) and air-quenched. Other samples of the same materials were heated to the point where the maximum of the effect was evidenced and air-quenched. Those samples air-quenched before the exothermic effect showed no crystalline X-ray pattern; those air-quenched at the maximum of the effect showed a faint but identifiable pattern of crystalline $\gamma = Al_2O_3$.[22] Samples air-quenched after the temperature of the sample had returned to the temperature of the reference material (at about 1,000° C) showed a faint X-ray pattern of mullite [23] in addition to $\gamma = Al_2O_3$. These results are shown in table 2 and figure 2.

TABLE 2.—*Crystalline phases indicated by X-ray patterns in the heat-treated kaolin minerals and gels giving an exothermic heat effect*

Material	Heated at 6° C per minute and air-quenched at—			
	Beginning of exothermic effect	Maximum of exothermic effect	1,000° C	1,200° C
Dickite	No pattern	γ-Al_2O_3	γ-Al_2O_3+mullite	Mullite.
Kaolinite	do	γ-Al_2O_3	γ-Al_2O_3+mullite	Do.
Coprecipitated gels:				
$2Al_2O_3.SiO_2$[a]	γ-Al_2O_3	γ-Al_2O_3+mullite	γ-Al_2O_3+mullite	α-Al_2O_3+mullite.
$Al_2O_3.SiO_2$	No pattern	γ-Al_2O_3+mullite	Mullite	Mullite.
$Al_2O_3.2SiO_2$[b]	do	Mullite	do	Do.
$Al_2O_3.4SiO_2$	do	do	do	Do.
Gel A[c]	do	γ-Al_2O_3+mullite	γ-Al_2O_3+mullite	Do.
Gel C[d]	(e)	γ-Al_2O_3	(e)	(e)

[a] No pattern after air-quenching at 903° C.
[b] The $Al_2O_3.SiO_2$ gel made from aluminum chloride and electrodialyzed gave the same results as the other coprecipitated gels of approximately this composition.
[c] Made by mixing gelatinous alumina and gelatinous silica and drying.
[d] Made by precipitating silica about fine particles of dried alumina gel in suspension.
[e] Not determined.

Heat treatment of the kaolin minerals at constant temperature below 925° C reduces the intensity of the exothermic heat effect to varying degrees, depending on the temperature and time of preheating. No strictly quantitative comparisons can be made since the size of the exothermic effect depends so much upon the centering of the thermocouple junctions in the sample and upon slight variations in the heating rate, but a relation is evident from figure 3 and table 3, which show the dependence of the size of the exothermic effect upon the preliminary heat treatment in samples of Zettlitz kaolin.[24] It is apparent that there is, in general, a decrease in the size of the exothermic effect with increase in the temperature of the preliminary heat treatment.

Also, the amount of acid-soluble alumina [25] in heat-treated samples, including both samples heated at constant temperatures and samples air-quenched upon reaching a given temperature, shows a relation to

[22] A modification of crystalline Al_2O_3 first described by Ulrich, Norsk Geol. Tids. **8**, 122 (1925). The X-ray patterns obtained were identical with those given by Hansen and Brownmiller, Am. J. Sci. **15**, 225-242 (1928), and by Brill, Z. Krist. **83**, 323-325 (1932).
[23] Although we have designated this pattern as mullite, there are not sufficient lines to decide whether the pattern is that of mullite or of sillimanite. On the basis of the discussion of Posnjak and Greig, J. Am. Ceram. Soc. **16**, 569-583 (1933), we have preferred to call it mullite.
[24] See also H. S. Houldsworth and J. W. Cobb, Trans. Ceram. Soc. **23**, 288 (1923-24).
[25] Our method of determination of Al_2O_3 soluble in HCl was that of Rhode, Keram. Rundschau **35**, 400 (1927), and our results agree well with hers.

the heat treatment which parallels that of the intensity of the exothermic effect and of the appearance of γ-Al_2O_3 (table 3).

TABLE 3.—*Relation of temperature and time of heat treatment to amount of "soluble Al_2O_3", X-ray pattern, and size of exothermic effect in samples of Zettlitz kaolin*

Preliminary heat treatment		Amount of "soluble Al_2O_3"	Crystalline phase indicated by X-ray pattern	Estimated exothermic effect at 950° C
Temp	Time			
°C	hr	*Percent*		
750	2	42.3	None	Large.
750	168	42.0	(a)	Do.
850	168	35.1	(a)	Medium.
880	26	38.5	(a)	Do.
880	74	26.4	γ-Al_2O_3	Do.
886	120	4.3	γ-Al_2O_3	Very small.
910	6	(a)	γ-Al_2O_3	Do.
910	24	5.5	γ-Al_2O_3	Do.
Air-quenched after heating to start of exothermic heat effect at 6° C/min.		43.5	None	Large.
Air-quenched after heating to maximum of exothermic heat effect at 6° C/min.		10.0	γ-Al_2O_3	None.

a Not determined.

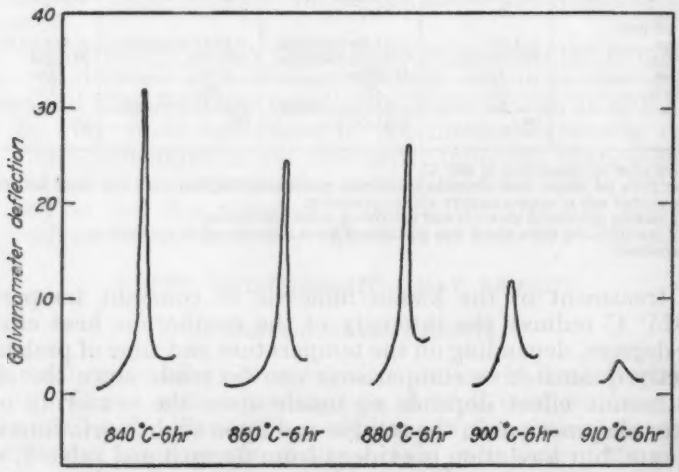

FIGURE 3.—*Relation of size of exothermic heat effect, beginning at 925° C in Zettlitz kaolin, to temperature of preliminary heat treatment.*

The coprecipitated gels described in section II gave exothermic effects at the same temperature and of approximately the same intensity as the kaolin minerals. The heating curves for the $Al_2O_3.SiO_2$ gel and $Al_2O_3.2SiO_2$ gel are given in figure 4. In the other coprecipitated gels the heat effects were of the same character and at the same temperature as the two shown in figure 4, but the effect was slightly less intense in the case of the $2Al_2O_3.SiO_2$ gel and much less in the case of the $4Al_2O_3.SiO_2$ and $Al_2O_3.4SiO_2$ gels. Heat treatments of these gels at constant temperatures just below 925° C resulted in reduced intensity of the heat effect just as in the kaolin minerals.

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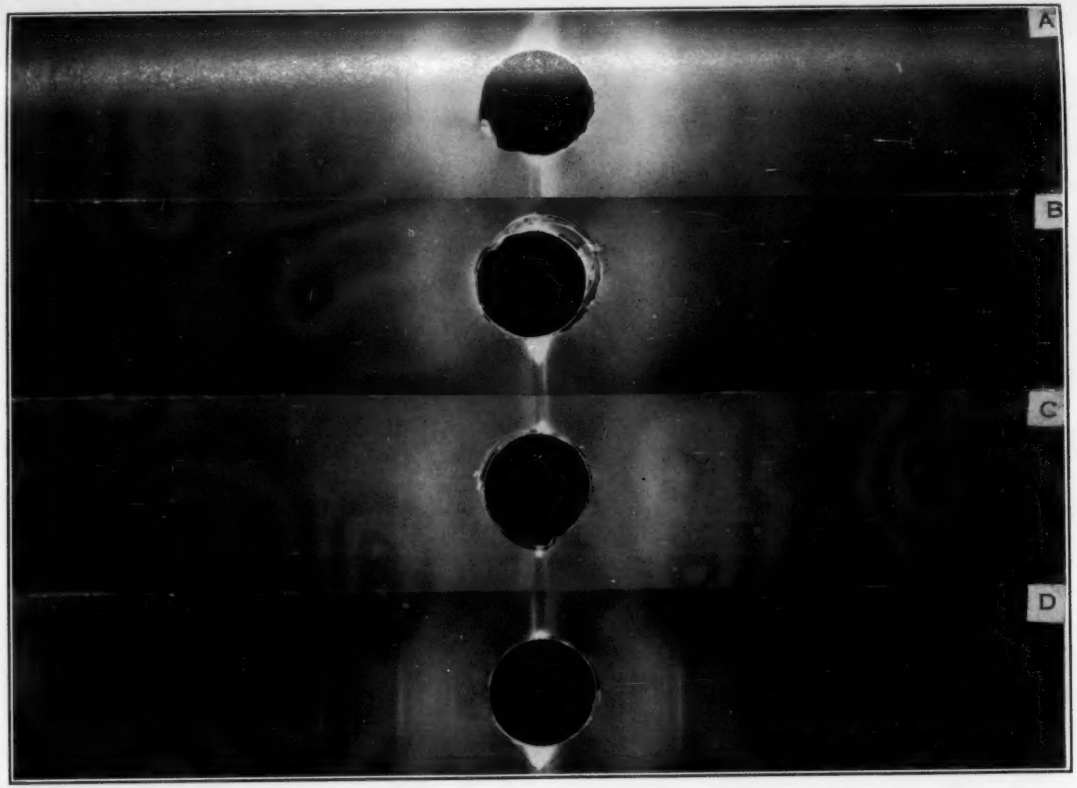

FIGURE 2.—*X-ray patterns of the kaolin minerals after heat treatment.*

A, Kaolinite (Zettlitz) heated to beginning of exothermic heat effect; B, Kaolinite (Zettlitz) heated to maximum of exothermic heat effect; C, Dickite heated above exothermic heat effect (about 1,000° C.); D, Mullite formed by heating kaolinite to 1,350° C. in 3½ hours.

Gels A and C gave small exothermic heat effects at the same temperature and of the same character as kaolin and the coprecipitated gels, but none were observed in gels B and D.

X-ray patterns were made of samples of these gels (except the $4Al_2O_3.SiO_2$ and gels B and D) which had been air-quenched immediately before the exothermic effect began and immediately after the maximum of the effect was reached. The results are given in table 2. In addition, samples of the $Al_2O_3.2SiO_2$ gel were air-quenched from several intermediate temperatures between the start and maximum of the exothermic heat effect, and X-rayed. These all showed mullite as the only crystalline phase, the patterns increasing in intensity with increasing temperature.

The crystallization of γ-Al_2O_3 from amorphous forms of Al_2O_3 takes place at much lower temperatures when only Al_2O_3 is present than it does when Al_2O_3 is associated with a considerable amount of SiO_2 (as in dehydrated kaolin) as is shown by the following experiments.

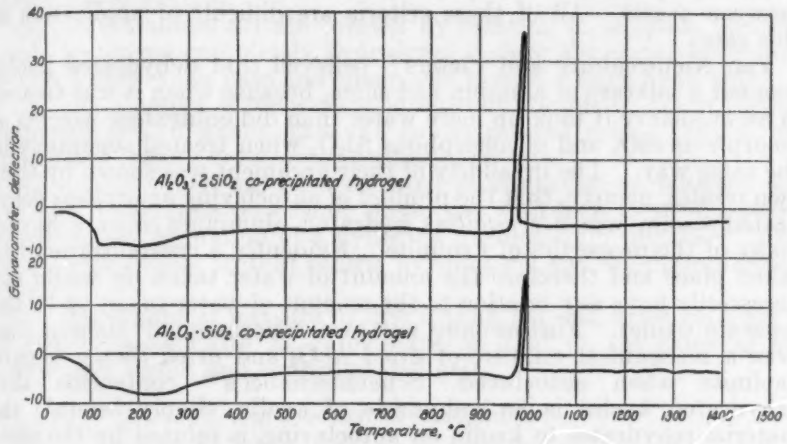

FIGURE 4.—*Heating curves of synthetic alumina-silica gels.*

Samples of amorphous Al_2O_3 gel (prepared by precipitating a solution of $AlCl_3$ with NaOH in the presence of phenol red as an indicator) were heated at 6° C/min to certain temperatures, air-quenched and X-rayed. Faint patterns of γ-Al_2O_3 were obtained from samples air-quenched from 600 and 700° C, and much stronger patterns from 800 and 900° C samples. All these temperatures are in the temperature range in which dehydrated kaolin and coprecipitated gels are still amorphous. The formation of γ-Al_2O_3 evidently occurs over a broad range of temperature since a differential heating curve shows no heat effect associated with the phase change. Other samples of amorphous Al_2O_3 (prepared by heating aluminum nitrate for 16 hours at 500° C) showed two broad exothermic heat effects, one beginning at about 725° C and ending at about 800° C, the other beginning at about 1,000° C and ending at about 1,050° C. The first of these effects [26] is due to the crystallization of γ-Al_2O_3 from amorphous Al_2O_3, as evidenced by X-ray patterns of samples air-quenched after heating to

[26] The second effect is due to the inversion of γ-Al_2O_3 to corundum.

700 and 800° C, which gave no pattern and the pattern of γ-Al_2O_3, respectively.

Differential heating curves of amorphous SiO_2 gel showed no heat effects up to 1,300° C, nor did samples air-quenched from temperatures up to 1,300° C show any crystallinity.

(b) THE NATURE OF DEHYDRATED KAOLIN

The question mentioned previously as to whether dehydrated kaolin is to be considered a mixture of amorphous Al_2O_3 and amorphous SiO_2, or an amorphous aluminum silicate compound, is a difficult one to answer conclusively. Since dehydrated kaolin is amorphous it is certainly not a compound with the ionic lattice characteristic of the crystalline state. The criteria of an amorphous compound, if such an entity exists, must be: (1) Random arrangement of the units of the compound; (2) lack of definite melting point; (3) definite proportions of component atoms; (4) shared-electron bonds between atoms. All of these criteria are difficult of application in this case.

Van Nieuwenburg and Pieters [27] believed that dehydrated kaolin was not a mixture of alumina and silica, because when it was treated in an autoclave it took up more water than did equivalent weights of amorphous SiO_2 and of amorphous Al_2O_3 when treated separately in the same way. The invalidity of their argument was shown by their own results, namely, that the product of autoclaving *amorphous* dehydrated kaolin was a *crystalline* hydrated aluminum silicate having many of the properties of kaolinite. Evidently a crystallization had taken place and therefore the amount of water taken up would not necessarily have any relation to the amount of water taken up by the separate oxides. Furthermore our own experiments [28] showed that even a mechanical mixture of dried Al_2O_3 and dried SiO_2 gels gave kaolinite when autoclaved. Schachtschabel's [29] contention that dehydrated kaolin is an anhydride of kaolin, simply because the material rehydrates to kaolin on autoclaving, is refuted by the same facts.

The authors believe that the mixture hypothesis is a simpler and more probable explanation of the results given in this paper. Such a mixture would necessarily be an exceedingly intimate one, possibly even a molecular dispersion of alumina in silica, differing both from a gross mechanical mixture and from a true chemical compound. The following line of reasoning is given in support of this viewpoint as opposed to the amorphous compound hypothesis.

Dehydrated kaolin and coprecipitated gels, for example $Al_2O_3.2SiO_2$ gel, resemble each other in the following points: (1) they both show a sharp, intense exothermic heat effect at 925 to 985° C; (2) they are both amorphous in the temperature range from about 700° C up to the start of the exothermic heat effect, when heated at 6° C/min; (3) heat treatment at constant temperature just below 925° C reduces, or completely eliminates, the heat effect in both cases; (4) the Al_2O_3 is practically completely soluble in HCl in both cases; (5) they both

[27] Rec. trav. chim. **48**, 27-36 (1929).
[28] Detailed report in preparation for publication.
[29] Chem. Erde **4**, 395-419 (1930).

form kaolin to approximately the same extent when heated with water in an autoclave at high temperatures (about 300° C.)[30]

In view of the facts it may be concluded that dehydrated kaolin and a coprecipitated gel of the same composition ($Al_2O_3.2SiO_2$) are very similar in internal structure and that evidence as to the nature of either may be considered evidence as to the nature of both. The following evidence is advanced for the hypothesis that both are mixtures and not chemical compounds:

(1) Gels A and C give exothermic effects at the same temperature and of the same character as the coprecipitated gels, though less intense. If it be assumed that any compound formation in the coprecipitated gels must take place by reaction between ions at the moment of precipitation, then compound formation in gels A and C would be highly improbable under the conditions of their preparation, and the exothermic effect observed could not be due to the decomposition of an aluminum silicate compound with simultaneous crystallization of γ-Al_2O_3.

(2) An aluminum silicate formed by reaction in aqueous solution would be almost completely hydrolyzed [31] since aluminum hydroxide is such a very weak base and silicic acid is such a very weak acid.

(3) The alumina is practically completely soluble in dilute HCl in both dehydrated kaolin and the coprecipitated gels. This is not true of any known crystalline aluminum silicate.

(4) Kaolin which has been calcined at temperatures between 550 and 800° C exhibits pozzolanic properties with lime solutions, owing largely to the formation of a hydrated monocalcium silicate.[32] This behavior is similar to that shown by silica gel and by diatomaceous silica.

(5) A mechanical mixture of dried Al_2O_3 gel and dried SiO_2 gel is converted to kaolinite on autoclaving at 312° C, the same as are dehydrated kaolin and coprecipitated gels.

(c) DISCUSSION OF RESULTS

The first crystalline material to be formed after the endothermic dissociation of kaolin is γ-Al_2O_3. When the sample is heated at moderately rapid rates (2° C or more per minute), this formation of crystalline material is closely related to the exothermic effect beginning at 925° C, as is shown by the X-ray patterns on samples removed from the furnace immediately before and immediately after the evolution of heat occurs. In samples heated for long periods γ-Al_2O_3 may be formed at temperatures as much as 50° C lower than this. This long heating at temperatures lower than 925° C causes partial or complete transformation of the amorphous Al_2O_3 to γ-Al_2O_3, and also causes partial or complete elimination of the exothermic effect in subsequent heatings.

Since the formation of γ-Al_2O_3 in the dehydrated kaolin takes place rapidly with a violent evolution of heat, while in the amorphous forms of pure alumina crystallization of γ-Al_2O_3 takes place over a long temperature interval at much lower temperatures, it is justifiable to conclude that the amorphous silica has a retarding action on this crystallization. We may assume that in pure amorphous alumina

[30] Rec. trav. chim. 48, 27-36 (1929).
[31] Compare H. N. Holmes, Ind. Eng. Chem. 17, 280-282 (1925).
[32] Report of the Building Research Board (Great Britain) p. 22 and 32 (1930).

there is a random structure and consequently individual molecules have different activities during heating. The change to the crystalline form, therefore, takes place gradually over a wide range of temperatures. In the dehydrated kaolin minerals, or in intimate mixtures of amorphous alumina and silica, however, the activity of the alumina molecules presumably is restrained by the rigid silica structure so that all the Al_2O_3 molecules have the same activity at a given temperature, and when, with increasing temperature the activity of all the Al_2O_3 molecules exceeds a certain "threshold value", the crystallization of γ-Al_2O_3 takes place very rapidly throughout the whole mass. This "threshold value" might be considered analogous to the energy of activation in gaseous reactions.

A similar case of repression of a phase change in the solid state by the presence of silica was observed by Geilmann, Klemm, and Meisel[33] in the mineral nontronite ($Fe_2O_3.3SiO_2.5\pm H_2O$). When this mineral is dehydrated, γ-Fe_2O_3 and amorphous SiO_2 are formed, and on further heating the γ-Fe_2O_3 inverts to α-Fe_2O_3 only at temperatures above 1,000° C, whereas pure γ-Fe_2O_3 inverts to α-Fe_2O_3 around 600° C. The investigators ascribe the stabilization of the lower temperature form to the effect of the rigid amorphous silica structure.

Some experiments of our own on the relative crystallizability of Fe_2O_3 gels and coprecipitated $Fe_2O_3.2SiO_2$ gels confirm the hypothesis of the restraining effect of silica on crystallization. Pure Fe_2O_3 gel when heated at 6° C/min to temperatures as low as 400° C gave an X-ray pattern of α-Fe_2O_3, whereas the $Fe_2O_3.2SiO_2$ gel still failed to show any crystallization when heated to 800° C at the same rate.

The rigidity of the structure in the amorphous forms of silica (glass and gel) is shown by the resistance of these forms to flow and the sluggishness with which they crystallize even when heated to very high temperatures.[34] A sample of silica gel, for instance, which we heated to 1,300° C at 6° C/min failed to show any X-ray pattern of a crystalline material.

The data in table 2 show that the coprecipitated gels resemble dehydrated kaolin in remaining amorphous up to the start of the exothermic heat effect, but differ in the crystalline phase present after the heat evolution has taken place, namely, γ-Al_2O_3 in the case of kaolin and mullite in the case of the gels (mullite+γ-Al_2O_3 in the case of the gels high in Al_2O_3). However, table 2 shows also that in kaolin heated to temperatures only slightly past the maximum of the heat effect, mullite is already present in crystals large enough to diffract X-rays. These data indicate that γ-Al_2O_3 formation is an intermediate step in mullite formation in kaolin; in fact, it appears to have a sort of "trigger action" with respect to mullite formation. Since this is the case in kaolin, it might be assumed that γ-Al_2O_3 is formed momentarily as an intermediate compound in the case of the gels. If this be true, the reaction to form mullite must be extremely rapid, for samples of gels air-quenched from temperatures intermediate between the start and maximum of the exothermic heat effect showed mullite as the only crystalline phase.

[33] Naturwissenschaften **20**, 639-640 (1932).
[34] Sosman, The Properties of Silica, p. 97-99, 473-475. (The Chemical Catalog Co., New York, N. Y.)

The internal structure of the material appears to determine which compound is formed. As shown by Gruner [35] the structure of the kaolin minerals is essentially lamellar. After dehydration with accompanying loss of crystal structure, the arrangement of the Al_2O_3 and SiO_2 molecules in the dehydrated kaolin is such that when crystallization begins, γ-Al_2O_3 forms first, followed shortly by mullite, while in the coprecipitated gels the molecular arrangement is such that mullite is the first observable crystalline phase formed.[36]

The intensity of the exothermic effect depends in part upon the intimacy of contact between the alumina and silica. In the $Al_2O_3.2SiO_2$, $Al_2O_3.SiO_2$, and $2Al_2O_3.SiO_2$ coprecipitated gels the exothermic effect is of about the same magnitude as in the kaolin minerals. The $4Al_2O_3.SiO_2$ and $Al_2O_3.4SiO_2$ gels show small heat effects. In the former the small amount of silica present is sufficient to keep only a part of the Al_2O_3 from crystallizing until 925° C, most of the Al_2O_3 crystallizing over a broad temperature range below 925° C without observable heat effect. In the latter case there is sufficient silica present, but the amount of Al_2O_3 is small and therefore the heat effect is small. The optimum ratio of Al_2O_3:SiO_2 for a large heat effect appears to lie between 1:1 and 1:2. In gels A and C the exothermic effects are of the same character and at the same temperature as in the coprecipitated gels but much less intense. This fact indicates that the character of the contact of the Al_2O_3 and SiO_2 in these two gels is the same as in the coprecipitated gels, but that the extent of contact is less.

V. SUMMARY

When the kaolin minerals, kaolinite and dickite, are heated at rates from 5 to 30° C/min there are two large and significant heat effects. The lower one, a broad but intense endothermic effect, is associated with the loss of water and the dissociation into an exceedingly intimate mixture of amorphous alumina and amorphous silica. The upper one, a sharp and intense exothermic effect, is associated with the formation of γ-Al_2O_3 from amorphous Al_2O_3. The evidence supports the conclusion that the formation of γ-Al_2O_3 at much higher temperatures in the kaolin minerals than in amorphous alumina is due to the restraining action of the rigid amorphous SiO_2 network on the crystallization of the Al_2O_3. In synthetic alumina-silica gels an exothermic effect at the same temperature and of the same character is observed with crystallization of mullite (or of mullite and γ-Al_2O_3) instead of γ-Al_2O_3. Apparently the nature of the resultant crystalline phase depends upon the internal structure of the material.

WASHINGTON, March 23, 1935.

[35] See footnote 4, p. 616.

[36] Since by Hess' law the heat evolved by the sum of the reactions:

$$\text{Amorphous } Al_2O_3 \rightarrow \gamma\text{-}Al_2O_3 \quad (1)$$
$$\gamma\text{-}Al_2O_3 + \text{amorphous } SiO_2 \rightarrow \text{mullite} \quad (2)$$

is the same as that evolved by the reaction:

$$\text{Amorphous } Al_2O_3 + \text{amorphous } SiO_2 \rightarrow \text{mullite} \quad (3)$$

and since the intensity of the exothermic heat effect is approximately the same for both kaolin and the $Al_2O_3.2SiO_2$ gel, i.e., ΔH for eq 1 = ΔH for eq 3, it can be deduced that ΔH for eq 2 is very small.

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MULTIPLETS AND TERMS IN THE FIRST TWO SPECTRA OF COLUMBIUM

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ABSTRACT

In the decade which has passed since the first indications of structure in these spectra were found, efforts have been made to improve the fundamental data so that the analyses might be extended. Careful estimates of relative intensities and accurate measurements of wave lengths have been compiled for about 3000 Cb I lines and 2000 Cb II lines. Results are now reported for the principal multiplets found in each spectrum. They reveal sextet and quartet terms for Cb I, quintet and triplet terms for Cb II, and account for most of the stronger lines. The normal state of neutral Cb atoms is represented by $(4d^4 5s)\,{}^6\mathrm{D}$ and for singly ionized atoms by $(4d^4)\,{}^5\mathrm{D}$.

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I. INTRODUCTION

Three multiplets involving sextet terms of the arc spectrum of columbium (Cb I) were published [1] in 1924, and five quintet-system multiplets for the spark spectrum (Cb II) were announced [2] in 1926. The theory of spectral structure predicted that the Cb I spectrum would exhibit terms belonging to sextet, quartet, and doublet systems, while the Cb II spectrum would be fully accounted for by quintet, triplet, and singlet terms. Although this was known even before the first regularities were discovered in Cb spectra, no further classification of Cb lines has appeared in a decade characterized by an avalanche of such regularities in other spectra. The reasons for this delay in further progress with analysis of Cb spectra were anticipated in the first paper referred to. These spectra are extremely rich in lines and the precision of the published wave lengths was not sufficient for unambiguous use of the combination principle, nor were the intensity estimates of arc and spark lines reliable enough for discrimination of ionization stages. No data existed for the absorption spectrum nor for furnace spectra at various temperatures, the results of which have been so helpful in the analysis of other complex spectra. Furthermore, the published Zeeman effects which gave the clue in the interpretation of the first regularities in these spectra were entirely inadequate for the extension of these analyses. Finally, the general experience that heavier ele-

[1] W. F. Meggers, J. Wash. Acad. Sci. **14**, 442 (1924).
[2] W. F. Meggers and C. C. Kiess, J. Opt. Soc. Am. **12**, 432 (1926).

ments show larger separations of sublevels in polyfold terms with consequent overlapping and perturbation of intervals, intensities, and magnetic splitting made it imperative to obtain improved and more complete descriptive data for these spectra before proceeding with the analyses of their structures. A considerable part of the required material is now at hand, and its analysis has resulted in the discovery and interpretation of a large number of atomic energy states characteristic of the neutral and of the singly ionized atoms of columbium. Although the spectral-line classifications are still far from complete, a majority of the strong lines in each spectrum is now accounted for and the results may be useful in connection with other investigations. In the present paper only those results are given which have been established and interpreted with a fairly high degree of certainty. The remainder are reserved for later publication together with observations of Zeeman effects essential for their interpretation.

II. DATA OF Cb SPECTRA (Z=41, M=93.3)

No wave length measurements of columbium have been published since those of Exner and Haschek [3] in 1912. Their arc and spark lists contain several thousand lines (7046.9 to 2155.68 A) and, although the errors do not often exceed 0.05 A, they are occasionally as large as 0.10 A. In such complex spectra the combination principle can be applied with confidence only if the errors in wave length values are less than 0.01 A, and the use of less precise values inevitably leads to hopelessness and despair in separating the real "constant differences" from the spurious ones. Furthermore, it is usually impossible to tell by comparing the published intensity values for arc and spark lines whether they belong to neutral or to ionized atoms and so the confusion in analysis is multiplied by chaos. After wasting many hours in attempting to extend the analysis with inadequate data, it became obvious that success depended on obtaining reliable basic facts concerning columbium spectra.

In 1927 Dr. C. W. Balke kindly presented some rods of columbium metal of high purity for spectroscopic investigations. With this material the arc and spark spectra have been accurately measured from 2000 to 12000 A, the furnace spectra and hyperfine structures have been studied by King,[4] and preliminary observations of Zeeman effects have been made.

The results of the furnace investigations have already been published, and the remainder should be published in the near future. The present paper excerpts only a fraction of the complete results but includes most of the stronger lines. It suffices here to state that a complete separation of Cb I, Cb II, and Cb III lines has been obtained and that the average probable error of wave length measurements is less than 0.01 A for more than 3000 Cb I lines and approximately 2000 Cb II lines.

In 1912 Jack [5] published observations of the Zeeman patterns for about 100 lines of Cb (2600 to 4700 A). These deserve the credit for revealing the first regularities in Cb I and Cb II spectra, but

[3] Die Spektren der Elemente bei Normalen Druck, 2 and 3, Deuticke, Wien (1911 and 1912).
[4] A. S. King, Astrophys. J. **73**, 441 (1931).
[5] Proc. Roy. Irish Acad. Dublin **30**, 42 (1912).

unfortunately they are not sufficiently numerous or precise to complete the analysis. Some preliminary observations made at this bureau indicate that most of the splitting factors deviate from Landé values and that still more extensive and accurate determinations are desirable. Since this program must be deferred to the future, a decision was made to present without further delay a portion of the new results as a group of selected multiplets and identified spectral terms characteristic of Cb I and Cb II spectra.

III. MULTIPLETS AND TERMS

It was the fashion some years ago to present all new spectral regularities in multiplet form, but the more recent custom is to give a list of classified lines and one of spectral terms. Each presentation has its advantages, but in this case we have elected the first in order to exhibit the interval, intensity, and combination rules for the principal groups of lines in the first two spectra of columbium. For each spectrum we give a multiplet table in which the term symbols and level values appear in the margins. The observed combinations are represented by measured wave lengths, estimated relative intensities (in parentheses), and by vacuum wave numbers.

The multiplet table is followed by a term table in which successive columns contain electron configurations, term symbols, level values and separations. Since, at the present time, it is impossible to assign absolute values to the spectral terms because no series have been found in these spectra, the term values are relative and based upon the assumption that the ground level or normal state has the value 0.00.

1. Cb I

The first spectrum of columbium arises from five valence electrons, and the theoretically possible low terms are those indicated in table 1, the last being the lowest of each group. Only ^{4,6}(D) ($4d^4 5s$) and ^{4}(F)($4d^3 5s^2$) have been identified with certainty thus far, but there can be no doubt that ^{6}(D)($4d^4 5s$) represents the normal state of the neutral Cb atom.

TABLE 1.—*Low terms of the* Cb I *spectrum*

Electron configuration	Terms
$4d^3 5s^2$	^{2}(D) ^{2}(PDFGH) ^{4}(PF).
$4d^4 5s$	^{2}(SDG) ^{2,4}(PF) ^{2}(SDFGI) ^{2,4}(PDFGH) ^{4,6}(D).
$4d^5$	^{2}D ^{2}(PDFGH) ^{4}(PF) ^{4}(SDFGI) ^{4}(DG) ^{6}S.

Remembering that terms from configurations in which a single penetrating s electron, interacting with an atomic nucleus having a mechanical moment of spin, show the largest hyperfine splitting [6] it was observed that most of the combinations with ^{4,6}(D)($4d^4 5s$) were complex lines (designated c or cw). Indeed, some of the ^{4}D levels were found on this assumption, and the fact that they exhibit large hyperfine splitting may be regarded as confirming their identity.

[6] W. F. Meggers and Kelvin Burns, J. Optical Soc. Am., **14**, 453 (1927).

TABLE 2.—*Multiplets*

Term symbol...		$a^6D_{9/2}$	$a^6D_{7/2}$	$a^6D_{5/2}$	$a^6D_{3/2}$	$a^6D_{1/2}$	$a^4F_{7/2}$
Value.....		0.00	154.19	391.99	695.25	1050.26	1142.79
Term symbol	Value						
		5094.40(10c)	5134.751(40)				
$z^6D_{11/2}$	19623.96	19623.94	19469.82				
		5057.999(40)	5097.764(5c)	5160.335(50)			5368.390(4)
$z^6D_{9/2}$	19765.20	19765.17	19611.00	19373.20			18622.39
			5039.032(40)	5100.161(30)	5180.305(50)		5303.272(3)
$z^6D_{7/2}$	19993.78		19839.56	19601.78	19298.52		18851.05
				5017.743(40c)	5095.298(80c)	5189.197(20)	
$z^6D_{5/2}$	20315.74			19923.74	19620.48	19265.45	
					4988.972(40)	5078.959(150)	
$z^6D_{3/2}$	20733.88				20038.64	19683.60	
		4168.121(250c)	4195.096(80)				
$y^6F_{11/2}$	23984.87	23984.89	23830.66				
		4137.090(200)	4163.657(250)	4205.308(120)			4342.459(7)
$y^6F_{9/2}$	24164.79	24164.79	24010.60	23772.80			23021.98
			4123.811(400)	4164.661(300)	4217.946(150c)		
$y^6F_{7/2}$	24396.80		24242.60	24004.81	23701.57		
				4100.918(600c)	4152.576(400c)	4214.732(100c)	
$y^6F_{5/2}$	24769.91			24377.93	24074.67	23719.64	
					4079.723(1000c)	4139.701(400cw)	
$y^6F_{3/2}$	25199.81				24504.57	24149.55	
						4058.931(2000c)	
$y^6F_{1/2}$	25680.36					24630.10	
		4116.894(50)	4143.201(80c)	4184.440(50c)			
$z^6P_{7/2}$	24283.34	24283.33	24129.15	23891.35			
			4099.066(30)	4139.430(90c)	4192.065(100c)		
$z^6P_{5/2}$	24543.13		24388.95	24151.13	23847.90		
				4078.343(6)	4129.429(100c)	4190.889(150c)	
$z^6P_{3/2}$	24904.86			24512.87	24209.62	23854.59	
		3862.927(20c)	3860.074(20)				4041.392(1)
$y^6D_{9/2}$	25879.81	25879.80	25725.65				24736.99
		3835.177(40)	3858.00(1)	3893.734(40)			
$y^6D_{7/2}$	26067.06	26067.05	25912.84	25675.04			
			3811.035(50)	3845.900(40)	3891.303(60)		
$y^6D_{5/2}$	26386.36		26232.17	25994.37	25691.08		
				3781.017(80)	3824.882(100)	3877.558(60)	
$y^6D_{3/2}$	26832.43			26440.43	26137.21	25782.15	
					3740.845(40)	3791.209(300r)	
$y^6D_{1/2}$	27419.62				26724.36	26369.35	
		3765.074(40)	3787.064(150)				3934.405(20)
$z^6D_{9/2}$	26552.40	26552.39	26398.21				25409.64
		3742.393(200r)	3764.115(25)	3798.127(300r)			3909.664(4)
$z^6D_{7/2}$	26713.30	26713.31	26559.15	26321.32			25570.43
			3726.235(250)	3759.556(200r)	3802.928(400r)		
$z^6D_{5/2}$	26983.34		26829.14	26591.36	26288.09		
				3697.850(200)	3739.804(300r)	3790.138(200r)	
$z^6D_{3/2}$	27427.07			27035.08	26731.80	26376.80	
					3664.691(80)	3713.017(300r)	
$z^6D_{1/2}$	27974.88				27279.59	26924.64	
		3535.304(400c)	3554.667(80)	3584.972(100)			3684.175(1)
$y^6P_{7/2}$	28278.25	28278.06	28124.03	27886.29			27135.42
			3507.960(80)	3537.475(150)	3575.850(200)		
$y^6P_{5/2}$	28652.66		28498.48	28260.70	27957.43		
				3497.815(30)	3535.304(400c)	3580.276(400r)	
$y^6P_{3/2}$	28973.12			28581.13	28278.06	27922.87	

in the Cb I spectrum

$a^4F_{3/2}$ 1586.90	$a^4F_{5/2}$ 2154.11	$a^4F_{7/2}$ 2805.36	$a^4D_{3/2}$ 8410.90	$a^4D_{5/2}$ 8705.32	$a^4D_{7/2}$ 9043.14	$a^4D_{9/2}$ 9497.52
			8915.76(4w)			
			11213.02			
				9039.18(7c)		
5499.531(7)				11059.92		
18178.33						
5431.253(12c)	5603.924(7)				9129.42(7w)	
18406.85	17839.70				10950.60	
5337.872(4c)	5504.581(20c)	5709.326(12)				9241.0(15cw)
18728.86	18161.66	17510.36				10818.4
	5380.705(4c)	5576.157(15c)				
	18579.77	17928.53				
4427.866(1)						
22577.92						
4382.856(9c)						
22809.79						
	4420.455(10)	4551.520(3)				
	22615.78	21964.54				
		4464.151(20)				
		22394.41				
		4370.361(15)				
		22875.00				
4404.740(1)						
22696.46						
	4465.232(4)					
	22388.99					
	4394.229(3)	4523.727(5)				
	22750.75	22099.48				
4083.776(5)						
24480.25						
	4125.571(12)					
	24232.26					
3959.977(4)	4051.000(6)	4160.807(8)			5619.78(1h)	
25245.55	24678.32	24027.05			17789.36	
		4061.540(10)				
		24614.28				
			5510.695(1h)			
			18141.50			
3978.753(12)						
25126.42						
3936.442(10)	4026.384(6)			5469.547(5c)	5572.519(2)	
25396.47	24829.19			18277.98	17940.24	
	3955.681(20)	4060.320(10)			5437.998(2c)	
	25272.97	24621.67			18384.02	
	3871.763(5)	3971.932(15)				
	25820.73	25169.57				
3745.476(6)					5197.37(2c)	
26691.32					19235.16	
3693.667(4)	3772.721(3)					5219.09(15cw)
27065.69	26498.57					19155.11

TABLE 2.—*Multiplets in the*

Term symbol..		$a^6D_{9/2}$	$a^6D_{7/2}$	$a^6D_{5/2}$	$a^6D_{3/2}$	$a^6D_{1/2}$	$a^4F_{7/2}$
Value.....		0.00	154.19	391.99	695.25	1050.26	1142.79
Term symbol	Value						
		5320.205(3)					5664.698(100)
$z^4D^0_{5/2}$	18791.09	18791.05					17648.31
		5251.629(15c)	5294.473(2)	5362.003(6)			5586.987(30)
$z^4D^0_{3/2}$	19036.57	19036.43	18882.38	18644.58			17893.78
			5186.986(15)	5251.805(10)	5336.797(6)		5467.410(3)
$z^4D^0_{1/2}$	19427.90		19273.67	19035.79	18732.63		18285.13
				5120.297(20)	5201.289(3)	5298.951(4)	
$z^4D^0_{-1/2}$	19916.69			19524.69	19221.41	18866.42	
		4971.917(10c)					5271.526 (60c)
$y^4D^0_{7/2}$	20107.36	20107.37					18964.58
		4904.534(25)	4941.905(2h)	5000.712(4)			5195.837(20)
$y^4D^0_{5/2}$	20383.62	20383.62	20229.48	19991.59			19240.83
			4833.362(40)	4889.551(7c)	4963.189(7)		5075.971(5c)
$y^4D^0_{3/2}$	20837.98		20683.77	20446.08	20142.73		19695.19
				4733.483(30c)	4802.442(9)	4885.765(5)	
$y^4D^0_{1/2}$	21512.18			21120.20	20816.94	20461.93	
		4300.989(100)	4329.732(20c)	4374.789(12c)			4523.409 (200)
$z^4F^0_{7/2}$	23243.87	23243.95	23089.65	22851.84			22101.04
			4268.667(15)	4312.454(25)	4369.618(8)		4456.800(30)
$z^4F^0_{5/2}$	23574.15		23419.95	23182.15	22878.88		22431.35
				4231.954(25)	4286.987(60)	4353.266(20)	
$z^4F^0_{3/2}$	24015.11			23623.14	23319.87	22964.83	
					4198.510(30)	4262.056(100)	
$z^4F^0_{1/2}$	24506.53				23811.29	23456.28	
		4345.315(20c)			4420.637(30c)		Masked
$z^4P^0_{3/2}$	23006.86	23006.84			22614.84		21864.07
			4248.658(8)		4292.035(20c)	4348.652(40cw)	4434.997(3)
$z^4P^0_{1/2}$	23684.44		23530.24		23292.44	22989.19	22541.62
		3855.456(15)			Masked		4033.192(40)
$y^4F^0_{9/2}$	25930.01	25929.94			25538.02		24787.27
			3858.953(40)		3894.704(10)	3941.266(40c)	4012.056(6)
$y^4F^0_{7/2}$	26060.65		25906.45		25668.65	25365.41	24917.86
					3878.818(40)	3924.995(40c)	3980.483(60c)
$y^4F^0_{5/2}$	26165.79				25773.77	25470.55	25115.50
						3883.141(80)	3937.437(150)
$y^4F^0_{3/2}$	26440.33					25745.08	25390.07
		3741.776(30c)	3763.492(40)				3908.971(40)
$x^4D^0_{7/2}$	26717.73	26717.71	26563.55				25574.96
		3711.343(60)	3732.702(5c)	3766.140(30c)			3875.764(20)
$x^4D^0_{5/2}$	26936.86	26936.79	26782.66	26544.87			25794.08
			3674.691(15)	3707.088(7c)	3749.248(1)		
$x^4D^0_{3/2}$	27350.70		27205.45	26967.70	26664.46		
				3674.787(40c)	3716.214(30c)		
$x^4D^0_{1/2}$	27596.74			27204.74	26901.48		
		3613.455(7c)	3633.717(20)				3769.145(20)
$y^4P^0_{5/2}$	27666.46	27666.48	27512.22				26523.71
		3598.343 (12vd)	3618.441(15)	3649.854(60)			3752.723(9)
$y^4P^0_{3/2}$	27782.57	27782.67	27628.36	27390.58			26639.77
			3533.667(40)	3563.624(80)	3602.561(60)		
$y^4P^0_{1/2}$	28445.33		28291.16	28053.34	27750.14		

Cb I *spectrum*—Continued

$a^4F_{2½}$ 1586.90	$a^4F_{3½}$ 2154.11	$a^4F_{4½}$ 2805.36	$a^4D_{0½}$ 8410.90	$a^4D_{1½}$ 8705.32	$a^4D_{2½}$ 9043.14	$a^4D_{3½}$ 9497.52
			9631.10(25c)	9912.21(15)		
			10380.19	10085.80		
5729.185(80)			9408.58(10)	9676.75(30c)	10003.80(25)	
17449.66			10625.68	10331.22	9993.44	
5603.512(30)	5787.523(80)			9323.50(20c)	9626.85(50w)	10067.34(15w)
17841.01	17273.77			10722.66	10384.77	9930.45
	5628.253(8c)	5842.467(30)				9595.03(30w)
	17762.58	17111.32				10419.21
			8547.25(20c)	8767.97(12)		
			11696.46	11402.02		
5318.597(50)			8350.04(10h)	8560.54(30c)	8815.56(100w)	
18796.74			11972.70	11678.30	11340.47	
5193.076(40c)	5350.723(100c)			8240.00 (50cw)	8475.98 (150cwl)	8815.56(100w)
19251.06	18683.88			12132.59	11794.81	11340.47
5017.362(3c)	5164.367(40c)	5344.160(200c)			8017.64(3c)	8320.93
19925.25	19358.08	18706.83			12469.07	12014.59 (500cwl)
4616.162(50)			6739.88(80)	6876.36(50)		
21656.97			14832.97	14538.57		
4546.820(150)	4667.224(50)			6723.62(100c)	6879.91(10c)	7102.01(20cw)
21987.25	21420.03			14868.84	14531.07	14076.65
4457.424(50)	4573.077(200c)	4713.496(80)			6677.33(100cw)	6886.32(30cw)
22428.21	21861.01	21209.76			14971.92	14517.55
	4472.536(40c)	4606.759(200c)				6660.84(200cw)
	22352.43	21701.17				15008.98
Masked			6849.34(20c)	6990.31(80)	7159.43(100)	
21419.96			14595.93	14301.58	13963.75	
4524.128(20)	4643.315(10)				6828.10(100)	7046.80(200)
22097.53	21530.33				14641.33	14186.93
4106.777(6)			5706.472(50)	5804.020(30)	5920.14(2c)	
24343.15			17519.11	17224.67	16886.82	
4084.856(40)	4181.784(6)			5760.329(80)	5874.681(40c)	
24473.78	23906.52			17355.32	17017.50	
	4163.474(40)	4279.53(5)			5838.608(100c)	5997.861(40cw)
	24011.66	23360.50			17122.63	16668.01
	4116.400(5)	4229.832(25)				5900.586 (150cw)
	24286.24	23634.97				16942.79
			5460.938(4c)	5550.179(2)		
			18306.80	18012.45		
3943.663(60)			5396.336(7c)	5483.485(8)	5586.987(30)	
25349.99			18525.96	18231.52	17893.78	
3878.966(20)	3966.246(150)			5359.183(7)	5458.043(10c)	5596.868(4h)
25772.79	25205.65			18654.39	18316.51	17862.19
3843.615(4)	3929.295(30c)	4032.523(150)			5388.299(6)	5523.569(25)
26009.82	25442.68	24791.39			18553.59	18099.22
				5272.480(5)		
				18961.14		
3816.342(15)				5240.392(5c)	5334.864(30c)	
26195.69				19077.25	18739.42	
3722.170(4)	3802.480(4)			5064.451(3c)	5152.623 (12cw)	5276.197(60cw)
26858.44	26291.19			19739.99	19402.20	18947.79

TABLE 2.—*Multiplets in the*

Term symbol..		$a^5D_{0\frac{1}{2}}$	$a^5D_{1\frac{1}{2}}$	$a^5D_{2\frac{1}{2}}$	$a^5D_{3\frac{1}{2}}$	$a^5D_{4\frac{1}{2}}$	$a^5F_{1\frac{1}{2}}$
Value.....		0.00	154.19	391.99	695.25	1050.26	1142.79
Term symbol	Value						
$x^5F_{1\frac{1}{2}}$	29779.44						3491.024(50) 28636.73
$x^5F_{2\frac{1}{2}}$	29987.45						3465.860(30) 28844.64
$x^5F_{3\frac{1}{2}}$	30161.56					3434.118(4) 29111.24	
$x^5F_{4\frac{1}{2}}$	30279.23					3420.287(4) 29229.96	
$w^5F_{1\frac{1}{2}}$	31707.94						3270.760(20) 30565.16
$w^5F_{2\frac{1}{2}}$	32139.78						3225.194(9) 30996.97
$w^5F_{3\frac{1}{2}}$	32451.99					3168.141(2h)	
$w^5F_{4\frac{1}{2}}$	32605.39					31555.15	
$w^5D_{0\frac{1}{2}}$	31907.75						3249.517(50) 30764.96
$w^5D_{1\frac{1}{2}}$	32248.69						
$w^5D_{2\frac{1}{2}}$	32545.51						
$w^5D_{3\frac{1}{2}}$	33003.89						
$v^5D_{1\frac{1}{2}}$	33717.01						3069.023(10) 32574.22
$v^5D_{2\frac{1}{2}}$	33872.18				3013.266(3h) 33176.93		3054.47(1) 32729.42
$v^5D_{3\frac{1}{2}}$	34168.94						
$u^5D_{1\frac{1}{2}}$	36016.26						2866.672(8) 34873.44
$u^5D_{2\frac{1}{2}}$	36180.11						2853.264(3) 35037.31
$u^5D_{3\frac{1}{2}}$	36334.21						
$t^5D_{0\frac{1}{2}}$	37536.56						2746.910 (20rv) 36393.80
$t^5D_{1\frac{1}{2}}$	37954.99						2715.692(8) 36812.14
$t^5D_{2\frac{1}{2}}$	38393.49						2683.714(5) 37250.75
$t^5D_{3\frac{1}{2}}$	38854.14					2644.444 (3c) 37803.89	
$x^5P_{0\frac{1}{2}}$	38730.17	2581.194(7) 38730.18					
$x^5P_{1\frac{1}{2}}$	38709.66						
$x^5P_{2\frac{1}{2}}$	38763.33						
$v^5F_{1\frac{1}{2}}$	38903.00						2647.500 (100R) 37760.25
$v^5F_{2\frac{1}{2}}$	39248.30						2623.510(30) 38105.52
$v^5F_{3\frac{1}{2}}$	39620.13						
$v^5F_{4\frac{1}{2}}$	40008.52						

Cb I *spectrum*—Continued

$a^4F_{3½}$ 1586.90	$a^4F_{3½}$ 2154.11	$a^4F_{4½}$ 2805.36	$a^4D_{0½}$ 8410.90	$a^4D_{1½}$ 8705.32	$a^4D_{2½}$ 9043.14	$a^4D_{3½}$ 9497.52
3546.031(12)			4678.48(20cw)	4743.839(15)	4821.116(3)	
28192.52			21368.50	21074.10	20736.31	
3520.055(40)	3591.790(9)			4697.468(30c)	4773.241(20c)	
28400.56	27833.36			21282.13	20944.29	
3498.608(30)	3569.464(40)	3654.430(10c)			4733.885(60cw)	4837.982(20cw)
28574.65	28007.45	27356.28			21118.41	20664.02
	3554.524(60)	3638.792(20c)				4810.584 (100cw)
	28125.16	27473.85				20781.70
3318.981(50)			4291.196(25)	4346.120(10)	4410.882(2)	
30121.09			23296.99	23002.58	22664.86	
3272.073(25)	3333.970(10)			4266.020(50)	4328.428(30c)	
30552.89	29985.68			23434.48	23096.61	
3238.975(2)	3299.608(30)	3372.100(10)			4270.691(50cw)	4355.245(5c)
30865.09	30297.94	29646.63			23408.85	22954.39
	3282.990(5)	3354.742(80)				4326.320 (100cw)
	30451.29	29800.02				23107.86
			4254.693(30)	4308.692(20c)		
			23496.87	23202.40		
			4193.828(10c)	4246.293(20)	4308.117(15c)	
			23837.87	23543.35	23205.49	
3229.189(4)	3289.460(8)			4193.420(1)	4253.693(50cw)	4337.561(12cw)
30958.62	30391.40			23840.19	23502.39	23047.97
	3240.582(3)	3310.467(25)			4172.34(1c)	4252.977(80cw)
	30849.78	30198.56			23960.64	23506.35
3111.446(20)						
32130.11						
3096.492(10)	3151.870(30)				4026.42(2)	
32285.27	31718.04				24829.0	
	3122.646(15)	3187.497(40)				4052.132(6c)
	32014.87	31363.54				24671.42
2903.648(10)			3621.450(1)	3660.498(2)		
34429.38			27605.36	27310.94		
2889.892(10)	2938.066(15)			3638.673(2c)	3683.973(5c)	
34593.25	34026.07			27474.74	27136.91	
	2924.822(10)	2981.634(15)			3663.167(8cw)	3725.195(20cw)
	34180.14	33528.90			27291.04	26836.63
			3432.419(15c)	3467.474(15)		
			29125.65	28831.24		
2748.848(20rv)			3383.802(15)	3417.867(15)	3457.800(20)	
36368.14			29544.10	29249.65	28911.87	
2716.104(10)	2758.610(50r?)			3367.382(25)	3406.138(40)	3459.703(25)
36806.55	36239.45			29688.16	29350.37	28895.97
	2723.990(10)	2773.197(50)			3353.509(15)	3405.417(60)
	36700.00	36048.84			29810.97	29356.59
			3297.286(8c)	3329.622(10)		
			30319.27	30024.83		
			3299.53(1)	3331.895(10)	3369.840(20d)	
			30298.7	30004.35	29666.51	
				3325.946(1)	3363.750(15d)	3415.984(30c)
				30058.02	29720.22	29265.78
2679.016(20r?)			3278.599(4)			
37316.07			30492.08			
2654.449(70R)	2695.039(40r)			3273.139(3)		
37661.41	37094.22			30542.94		
2628.495(20)	2668.290(40r)	2715.503(6)			3269.493(3c)	
38033.25	37466.06	36814.70			30576.99	
	2640.913(20vd)	2687.148(50r?)				3276.567(4)
	37854.43	37203.15				30510.99

TABLE 3.—*Terms of the* Cb I *spectrum*

Electron configuration	Term symbol	Term value	Level separation	Electron configuration	Term symbol	Term value	Level separation
$3d^44s$	$a^6D_{9/2}$	0.00		$d^3sp(^3F)$	$z^4F^0_{7/2}$	23, 243. 87	
			154. 19				330. 28
	$a^6D_{1/2}$	154. 19			$z^4F^0_{5/2}$	23, 574. 15	
			237. 80				440. 96
	$a^6D_{3/2}$	391. 99			$z^4F^0_{3/2}$	24, 015. 11	
			303. 26				491. 42
	$a^6D_{3/2}$	695. 25			$z^4F^0_{1/2}$	24, 506. 53	
			355. 01	$d^4p(^5D)$	$z^4P^0_{5/2}$		
	$a^6D_{4/2}$	1, 050. 26			$z^4P^0_{3/2}$	23, 006. 86	
$3d^34s^2$	$a^4F_{9/2}$	1, 142. 79					677. 58
			444. 11		$z^4P^0_{1/2}$	23, 684. 44	
	$a^4F_{7/2}$	1, 586. 90		$d^4p(^5D)$	$y^4F^0_{9/2}$	25, 930. 01	
			567. 21				130. 64
	$a^4F_{5/2}$	2, 154. 11			$y^4F^0_{7/2}$	26, 060. 65	
			651. 25				105. 14
	$a^4F_{3/2}$	2, 805. 36			$y^4F^0_{5/2}$	26, 165. 79	
$3d^44s$	$a^4D_{7/2}$	8, 410. 90					274. 54
			294. 42		$y^4F^0_{3/2}$	26, 440. 33	
	$a^4D_{5/2}$	8, 705. 32		$d^4p(^5D)$	$x^4D^0_{5/2}$	26, 717. 73	
			337. 82				219. 13
	$a^4D_{3/2}$	9, 043. 14			$x^4D^0_{3/2}$	26, 936. 86	
			454. 38				422. 84
	$a^4D_{3/2}$	9, 497. 52			$x^4D^0_{3/2}$	27, 359. 70	
$d^3sp(^5F)$	$z^6D^0_{9/2}$	19, 623. 96					237. 04
			141. 24		$x^4D^0_{1/2}$	27, 596. 74	
	$z^6D^0_{7/2}$	19, 765. 20		$d^3sp(^3P)$	$y^4P^0_{5/2}$	27, 666. 46	
			228. 58				116. 11
	$z^6D^0_{5/2}$	19, 993. 78			$y^4P^0_{3/2}$	27, 782. 57	
			321. 96				662. 76
	$z^6D^0_{3/2}$	20, 315. 74			$y^4P^0_{1/2}$	28, 445. 33	
			418. 14	$d^3sp(^3G)$	$z^4F^0_{9/2}$	29, 779. 44	
	$z^6D^0_{1/2}$	20, 733. 88					208. 01
$d^4p(^5D)$	$y^6F^0_{11/2}$	23, 984. 87			$z^4F^0_{7/2}$	29, 987. 45	
			179. 92				174. 11
	$y^6F^0_{9/2}$	24, 164. 79			$z^4F^0_{5/2}$	30, 161. 56	
			232. 01				117. 67
	$y^6F^0_{7/2}$	24, 396. 80			$z^4F^0_{3/2}$	30, 279. 23	
			373. 11	$d^3sp(^5F)$	$w^4F^0_{9/2}$	31, 707. 94	
	$y^6F^0_{5/2}$	24, 769. 91					431. 84
			429. 90		$w^4F^0_{7/2}$	32, 139. 78	
	$y^6F^0_{3/2}$	25, 199. 81					312. 21
			480. 55		$w^4F^0_{5/2}$	32, 451. 99	
	$y^6F^0_{1/2}$	25, 680. 36					153. 40
$d^4p(^5D)$	$z^6P^0_{7/2}$	24, 283. 34			$w^4F^0_{3/2}$	32, 605. 39	
			259. 79	$d^3sp(^5F)$	$w^4D^0_{9/2}$	31, 907. 75	
	$z^6P^0_{5/2}$	24, 543. 13					340. 94
			361. 73		$w^4D^0_{7/2}$	32, 248. 69	
	$z^6P^0_{3/2}$	24, 904. 86					296. 82
$d^4p(^5D)$	$y^6D^0_{9/2}$	25, 879. 81			$w^4D^0_{5/2}$	32, 545. 51	
			187. 25				458. 38
	$y^6D^0_{7/2}$	26, 067. 06			$w^4D^0_{3/2}$	33, 003. 89	
			319. 30	$d^3sp(^3P)$	$v^4D^0_{5/2}$		
	$y^6D^0_{5/2}$	26, 386. 36			$v^4D^0_{7/2}$	33, 717. 01	
			446. 07				155. 17
	$y^6D^0_{3/2}$	26, 832. 43			$v^4D^0_{3/2}$	33, 872. 18	
			587. 19				296. 76
	$y^6D^0_{1/2}$	27, 419. 62			$v^4D^0_{1/2}$	34, 168. 94	
$d^3sp(^5P)$	$z^6D^0_{9/2}$	26, 552. 40		?	$u^4D^0_{5/2}$		
			160. 90		$u^4D^0_{7/2}$	36, 016. 26	
	$z^6D^0_{7/2}$	26, 713. 30					163. 85
			270. 04		$u^4D^0_{3/2}$	36, 180. 11	
	$z^6D^0_{5/2}$	26, 983. 34					154. 10
			443. 73		$u^4D^0_{1/2}$	36, 334. 21	
	$z^6D^0_{3/2}$	27, 427. 07		$d^4p(^3F)$	$t^4D^0_{5/2}$	37, 536. 56	
			547. 81				418. 43
	$z^6D^0_{1/2}$	27, 974. 88			$t^4D^0_{7/2}$	37, 954. 99	
$d^3sp(^3P)$	$y^6P^0_{7/2}$	28, 278. 25					438. 50
			374. 41		$t^4D^0_{3/2}$	38, 393. 49	
	$y^6P^0_{5/2}$	28, 652. 66					460. 65
			320. 46		$t^4D^0_{1/2}$	38, 854. 14	
	$y^6P^0_{3/2}$	28, 973. 12		?	$x^4P^0_{5/2}$	38, 730. 17	
?	$z^4D^0_{5/2}$	18, 791. 09					−20. 51
			245. 48		$x^4P^0_{3/2}$	38, 709. 66	
	$z^4D^0_{7/2}$	19, 036. 57					53. 67
			391. 33		$x^4P^0_{1/2}$	38, 763. 33	
	$z^4D^0_{5/2}$	19, 427. 90		$d^4p(^3F)$	$s^4F^0_{9/2}$	38, 903. 00	
			488. 79				345. 30
	$z^4D^0_{3/2}$	19, 916. 69			$s^4F^0_{7/2}$	39, 248. 30	
$d^3sp(^3F)$	$y^4D^0_{5/2}$	20, 107. 36					371. 83
			276. 26		$s^4F^0_{5/2}$	39, 620. 13	
	$y^4D^0_{3/2}$	20, 383. 62					388. 39
			454. 36		$s^4F^0_{3/2}$	40, 008. 52	
	$y^4D^0_{1/2}$	20, 837. 98					
			674. 20				
	$y^4D^0_{3/2}$	21, 512. 18					

The nuclear moment of columbium has been determined from hyperfine structure by Ballard.[7] A value of $I=9/2$ is indicated, but this leads to wrong quantum numbers for some of the classified lines (e. g., 5344 and 6661 A).

The low even terms of Cb I named in table 1 combine with a great many higher odd terms which occur when a p electron is substituted in one of the listed configurations. A large number of these middle levels have been established but it is difficult at present to group them into terms and assign configurations. Thus far the guiding principles of these attempts have been interval and intensity rules, and comparison with the analogous spectrum of vanadium. The sextet system is well established, the quartet system somewhat less complete and certain, while the doublet system still remains unrecognized. The average deviations of an observed wave number from the corresponding term combination is 0.02 cm^{-1} for classified Cb I lines.

The raie ultime of columbium in low excitation sources where neutral atoms predominate is the line at 4058.931 A, which is classified as $(4d^4 5s)a^6D_{4½} - (4d^4 5p)y^6F^o_{5½}$.

[7] Phys. Rev., **46**, 806 (1934).

TABLE 4.—*Terms of the* Cb II *spectrum*

Electron configuration	Term symbol	Term value	Level separation	Electron configuration	Term symbol	Term value	Level separation
$4d^4$	a^5D_0	0.00		$4d^35p(^4F)$	$z^5F_1^1$	36731.78	
	a^5D_1	159.00	159.00		$z^5F_2^1$	36962.78	231.00
	a^5D_2	438.38	279.38		$z^5F_3^1$	37376.93	414.15
	a^5D_3	801.38	363.00		$z^5F_4^1$	37528.38	151.45
	a^5D_4	1224.85	423.47		$z^5F_5^1$	38024.33	495.95
$4d^35s(^4F)$	a^5F_1	2356.76		$4d^35p(^4F)$	$z^5D_0^1$	37298.20	
	a^5F_2	2629.10	272.34		$z^5D_1^1$	37480.02	181.82
	a^5F_3	3029.58	400.48		$z^5D_2^1$	37797.29	317.27
	a^5F_4	3542.53	512.95		$z^5D_3^1$	38216.38	419.09
	a^5F_5	4146.02	603.49		$z^5D_4^1$	38291.27	74.89
$4d^4$	a^3P_0	5562.25		$4d^35p(^4F)$	$z^3D_1^1$	34886.35	
	a^3P_1	6192.31	630.06		$z^3D_2^1$	35520.85	634.50
	a^3P_2	7261.33	1069.02		$z^3D_3^1$	36553.27	1032.42
$4d^4$	a^3F_2	7505.82		$4d^35p(^4F)$	$z^3G_3^1$	38684.94	
	a^3F_3	7900.67	394.85		$z^3G_4^1$	39335.29	650.35
	a^3F_4	8320.44	419.77		$z^3G_5^1$	40103.60	768.31
$4d^4$	a^3G_3	10247.08		$4d^35p(^4F)$	$z^3F_2^1$	38984.42	
	a^3G_4	10604.25	357.17		$z^3F_3^1$	39779.99	795.57
	a^3G_5	11047.15	442.90		$z^3F_4^1$	40231.97	451.98
$4d^35s(^4P)$	a^5P_1	10653.41		$4d^35p(^4P)$	$y^5D_0^1$	?	
	a^5P_2	10835.94	182.53		$y^5D_1^1$	43649.15	
	a^5P_3	11339.57	503.63		$y^5D_2^1$	43290.38	−358.70
$4d^35s^2$	b^3F_2	12805.96			$y^5D_3^1$	43887.10	596.72
	b^3F_3	13690.27	884.31		$y^5D_4^1$	44970.72	1083.62
	b^3F_4	13665.72	−24.55	$4d^35p(^4P)$	$z^5P_1^1$	43450.05	
$4d^35p(^4F)$	$z^5G_2^1$	33351.00			$z^5P_2^1$	44226.83	776.78
	$z^5G_3^1$	33919.24	568.24		$z^5P_3^1$	44771.55	544.72
	$z^5G_4^1$	34632.04	712.80	$4d^35p(^4P)$	$z^5P_0^1$	44936.01	
	$z^5G_5^1$	35474.22	842.18		$z^5P_1^1$	45374.95	438.94
	$z^5G_6^1$	36455.50	981.28		$z^5P_2^1$	46545.32	1170.37
				$4d^35p(^4P)$	$z^5S_2^1$	47072.88	

2. Cb II

When a columbium atom loses one electron it can be excited to emit another spectrum which is characteristic of four valence electrons. The low terms which may be expected in this case are indicated in table 5.

TABLE 5.—*Low terms of the* Cb II *spectrum*

Electron configuration	Terms
$4d^3\,5s^2$	^{1}(SDG) ^{3}(PF)
$4d^3\,5s$	^{1,3}(D) ^{1,3}(PDFGH) ^{3,5}(PF)
$4d^4$	^{1}(SDG) ^{3}(PF) ^{1}(SDFGI) ^{3}(PDFGH) ^{5}(D)

All of the quintet terms have been found, but only a portion of the triplet terms, and none of the singlets thus far. Here, as in Cb I, the terms arising from the configuration with a single s electron are outstanding in connection with hyperfine structure. Nearly all of the lines involving ^{5}(PF) ($4d^3\,5s$) show hyperfine structure in grating spectrograms, and some unclassified complex lines were suspected of belonging to ^{3}(PF) ($4d^3\,5s$) but a search for these terms was unsuccessful. However, it can be stated positively that ^{5}(D) $4d^4$ represents the normal state of the singly ionized Cb atom.

Transitions to the above-listed low even terms from higher excited odd terms represented by a p electron in the outer atomic structure account for the first spark spectrum of columbium. The establishment of these odd terms for Cb II is now practically complete for the quintet system, much less so for the triplet system, and entirely lacking for the singlets. Further search for the missing terms is considered a waste of time until more Zeeman effects are available.

When the spectra of ionized atoms are produced at atmospheric pressure by highly condensed sparks, it is commonly observed that most of the lines are broadened and somewhat unsymmetrical, the displacement being usually toward longer waves. Wave-length measurements from such spark spectrograms are thus affected by Stark effects and do not represent simple atomic constants. Since practically all of the spark lines here reported appeared also in arc spectrograms, the wave length values in table 6 represent measurements in arc spectra, but the intensities are estimated from spark spectrograms. The average deviation of observed wave numbers from term combinations is ± 0.04 cm^{-1} for classified Cb II lines.

The raie ultime for columbium in sources in which singly ionized atoms predominate is the line at 3094.171 classified as ($4d^3\,5s$) $^5F_5 - (4d^3\,5p)\ ^5G^0_6$. This is by far the strongest line in the Cb II spectrum, and even though it does not involve the normal state, it can be relied upon as the most persistent line because it involves the largest quantum numbers permitted in a simple s, p interchange of electrons.[8]

[8] W. F. Meggers and B. F. Scribner, Research J. NBS **13**, 657 (1934).

TABLE 6.—*Multiplets in the* Cb II *spectrum*

Term symbol	Value	a^5D_0 0.00	a^5D_1 159.00	a^5D_2 438.38	a^5D_3 801.38	a^5D_4 1224.85	a^5F_1 2356.76	a^5F_2 2629.10	a^5F_3 3029.58	a^5F_4 3542.53	a^5F_5 4146.02
			2691.774(60r)				2361.091(100)				
$z^5D_0^0$	37298.20		37139.21				34941.46				
		2667.300(30)	2678.663(10)	2698.866(100r)			2846.280(60)	2865.524(200r)			
$z^5D_1^0$	37480.02	37479.97	37320.98	37041.62			35123.28	34850.92			
			2656.076(80r)	2675.945(80r)	2702.197(70r)		2820.803(12)	2842.642(100r)	2875.386(300Rc)		
$z^5D_2^0$	37797.29		37638.34	37358.89	36995.97		35440.49	35168.22	34767.76		
				2646.258(100r)	2671.933(150r)	2702.521(40)		2807.170(8)	2841.141(100)	2883.168(400Rc)	
$z^5D_3^0$	38216.38			37777.97	37414.98	38991.53		35587.22	35186.80	34673.92	
					2666.595(40)	2697.067(300r)			2935.112(50)	2876.956(200)	2927.804(600Rc)
$z^5D_4^0$	38291.27				37489.87	37066.33			35261.70	34748.79	34145.33
		2721.632(6)	2733.464(10)	2754.523(40)			2908.236(200r)	2931.458(70)			
$z^5F_1^0$	36731.78	36731.80	36572.81	36293.22			34375.06	34102.77			
			2716.310(15)	2737.083(60)	2764.561(10)		2888.824(150r)	2911.740(300r)	2946.105(60)		
$z^5F_2^0$	36962.78		36803.76	36524.50	36161.45		34606.04	34333.70	33933.23		
				2706.395(40)	2733.258(40r)	2765.271(10)		2877.030(200r)	2910.580(400r)	2954.720(4)	
$z^5F_3^0$	37376.93			36938.58	36575.57	36152.16		34747.90	34347.38	33834.30	
					2721.986(150r)	2753.74(3)			2897.803(200r)	2941.536(500R)	2994.724(300c)
$z^5F_4^0$	37528.38				36727.02	36303.54			34498.82	33985.94	33382.35
						2716.63(200r)				2899.230(200r)	2950.878(800c)
$z^5F_5^0$	38024.33					36799.41				34481.84	33878.36
							3225.480(500Rc)	3254.070(200r)	3297.055(20)		
$z^5G_2^0$	33351.00						30994.22	30721.91	30321.40		
								3194.983(700R)	3236.403(300r)	3291.055(30)	
$z^5G_3^0$	33919.24							31290.06	30889.62	30376.67	
									3163.403(1000R)	3215.595(300rc)	3279.248(20c)
$z^5G_4^0$	34632.04								31602.41	31089.49	30486.04
						2918.916(3)				3130.780(1500Rc)	3191.096(200c)
$z^5G_5^0$	35474.22					34249.29				31931.69	31328.17
											3094.171(2000Rc)
$z^5G_6^0$	36455.50										32309.48
		2300.785(50)	2309.239(100)	2324.237(60)							
$z^5P_1^0$	43450.05	43450.02	43290.97	43011.74							
			2268.527(150)	2283.004(300)	2302.086(200)						
$z^5P_2^0$	44225.83		44067.81	43788.40	43425.47						
				2254.953(60)	2273.566(150)	2295.681(300)					
$z^5P_3^0$	44771.55			44333.05	43970.15	43546.61					

$z^4D_1^1$	34886. 35	2865.609(60) 34886.38	2878.739(8) 34727.27	2949.580(100) 35082.60	2879.360(15) 34719.54		3073.234(50) 32529.59	3099.179(100) 32257.28	3076.964(200) 32491.21		
$z^4D_2^1$	35520. 85		2827.071(50) 35361.91	2768.124(100r) 36114.90		2829.750(15) 35328.44	3014.438(15) 33164.04	3039.399(10) 32891.70	2862.100(100) 33526.66	3028.437(300c) 33010.75	
$z^4D_3^1$	36553. 27			2613.854(8) 38246.27	2538.877(5) 37883.63			2946.890(80) 33924.19	2803.810(15) 35655.27		
$z^4G_3^1$	38694. 94				2594.337(10) 38533.98	2623.170(6) 38110.46			2753.58(5) 36305.69	2793.044(80) 35792.70	
$z^4G_4^1$	39335. 29					2571.324(60) 38878.83				2734.360(15) 36560.83	2780.235(150c) 35957.60
$z^4G_3^1$	40103. 60										
$z^4P_2^0$	44936. 01			2224.667(30) 44936.53							
$z^4P_1^0$	45374. 95	2209.170(5) 45374.94	2210.917(20) 45215.96								
$z^4P_3^0$	46545. 32		2155.13(2) 46383.27	2168.188(4) 46106.04	2185.398(5) 45743.89						
$y^4D_1^1$	43649. 15	2290.269(5) 43649.12	2298.662(6) 43490.15	2313.524(15) 43210.79							
$y^4D_2^1$	43290. 35		2317.784(8) 43131.38	2332.896(10) 42852.01	2352.837(60) 42488.87						
$y^4D_3^1$	43887. 10			2300.854(10) 43448.72	2320.238(20) 43085.77	2343.271(10) 42662.30					
$y^4D_4^1$	44970. 72				2263.312(15) 44169.34	2295.223(60) 43745.83					

TABLE 6.—*Multiplets in the* Cb II *spectrum*—Continued

Term symbol / Value		a³P₁ 10653.41	a³P₂ 10835.94	a³P₀ 11339.57	a³P₀ 5562.25	a³P₁ 6192.31	a³P₂ 7261.33
Term symbol	Value						
z³D⁰₃	37298.20	3752.01(1) 26644.8				3213.912(3) 31105.77	
z³D⁰₂	37480.02	3726.58(10c) 26826.6	3752.08(1) 26644.3		3132.440(4) 31917.83	3195.216(5) 31287.77	
z³D⁰₁	37797.29	3683.0(10C) 27144.0	3707.96(60C) 26961.35	3378.50(1) 26458 7		3163.149(10) 31604.95	3273.888(15) 30535.95
z³D⁰₂	38216.38		Masked 27380.44	3719.63(25c) 26876.78			3229.567(100) 30955.00
z³D⁰₁	38291.27			3709.29(100C) 26951.70			
z³F⁰₄	36731.78				3207.341(20) 31169.50	3273.511(20) 30539.47	
z³F⁰₃	36962.78					3248.941(80) 30770.41	3365.883(10) 29701.38
z³F⁰₂	37376.93						3319.590(100) 30115.57
z³F⁰₁	37528.38						
z³F⁰₂	38024.33						
z³S⁰₁	47072.88	2744.97(20c) 36419.52	2758.807(50c) 36236.86	2797.693(100c) 35733.22		2445.402(2) 40880.68	
z³P⁰₂	43450.05	3048.216(80c) 32796.56	3065.260(100c) 32614.21		2638.591(7) 37887.73	2683.216(6) 37257.62	2762.48(3) 36188.69
z³P⁰₁	44226.83	2977.668(150c) 33573.56	2993.971(20c) 33390.75	3039.819(150c) 32887.15		2628.408(3) 38034.51	2704.417(5) 36965.60
z³P⁰₀	44771.55		2945.890(100c) 33935.70	2990.262(200c) 33432.16			
z³D⁰₃	34886.35				3409.191(100) 29324.09	3484.054(80) 28694.01	3618.89(4) 27624.92
z³D⁰₂	35520.85					3408.678(100) 29328.50	3537.625(40) 28259.50
z³D⁰₁	36553.27						3412.934(150) 29291.93

z⁴F⁸	44936.01	2916.091(8c) 34282.47	2894.436(20c) 34538.95		2511.004(100) 39812.72	2580.284(30) 38743.83 2551.382(120)	2622.952(20) 38113.62
z⁴F⁷	45374.95					39182.69 2477.379(150)	2544.802(200)
z⁴F⁶	46545.32			2839.62(7c) 35205.7		40353.05	39284.00
		3029.81(60d)	3046.67(6c)				
y⁴D⁷	43649.15	32995.79	32813.20			2604.753(4)	
		3063.128(40d)	3080.345(100c)	3128.915(10c)		37098.16	2729.524(2)
y⁴D⁶	43290.38	32636.93	32454.50	31950.73			36625.60
			3024.735(200c)	3071.547(90c)			
y⁴D⁵	43887.10		33051.15	32547.56			
				2972.568(200c)			
y⁴D⁴	44970.72			33631.15			

TABLE 6.—*Multiplets in the* Cb II *spectrum*—Continued

Term symbol value..		a^3F_2	a^3F_3	a^3F_4	a^3G_3	a^3G_4	a^3G_5	b^3F_2	b^3F_3	b^3F_4
Value		7505.82	7900.67	8320.44	10247.08	10604.25	11047.15	12805.96	13690.27	13665.72
Term symbol	Value									
		3335.245(10)								
$z^5D_1^1$	37480.02	29974.22								
		3300.337(6)	3343.903(4)		3628.70(2)				4146.99(4)	
$z^5D_2^1$	37797.29	30291.24	29896.61		27550.3				24106.98	
		3255.270(5)	3297.673(15)	3343.968(80)		3620.560(6)				4072.064(15)
$z^5D_3^1$	38216.38	31710.59	30315.71	29896.03		27612.19				24550.66
			3289.551(10)	3335.672(5)					4063.734(10)	4059.670(10)
$z^5D_4^1$	38291.27		30390.56	29970.38					24600.99	24625.61
		3420.633(80)						4178.396(6)		
$z^5F_1^1$	36731.78	29226.00						23925.91		
		3393.809(10)	3439.925(60)					4138.453(10)	4295.71(4)	
$z^5F_2^1$	36962.78	29456.99	29062.10					24156.83	23272.51	
		3346.760(30)	3391.593(9)	3440.589(120)	3684.932(4)			4068.712(5)	4220.598(15)	4216.228(50)
$z^5F_3^1$	37376.93	29871.09	29476.24	29056.50	27129.85			24570.89	23686.68	23711.23
			3374.252(50)	3422.770(5)	3664.47(2)	Masked			4193.80(10)	4189.475(1)
$z^5F_4^1$	37528.38		29627.72	29207.76	27281.3	26924.13			23838.03	23862.64
				3365.594(100)		3645.944(6)				4104.163(50)
$z^5F_5^1$	38024.33			29703.93		27419.95				24358.65
								4865.989(15)		
$z^5G_2^1$	33351.00							20545.09		
		3684.878(5)						4735.04(2)	4941.998(4)	
$z^5G_3^1$	33919.24	26413.46						21113.26	20229.10	
			Masked						4773.799(7)	4768.232(3)
$z^5G_4^1$	34632.04		26731.37						20941.84	20966.29
				3681.679(6)		4019.79(1)				4584.10(6)
$z^5G_5^1$	35474.22			27153.88		24869.92				21808.44
		3651.182(200)						4527.648(100)		
$z^3D_1^1$	34886.35	27380.62						22080.35		
		3568.510(30)	3619.514(200)		3955.549(3)			4401.172(50)	4579.446(100)	
$z^3D_2^1$	35520.85	28014.93	27620.17		25273.81			22714.86	21830.61	
		3441.663(10)	3489.093(90)	3540.961(250)		3852.624(6)			4372.645(40)	4367.966(100)
$z^3D_3^1$	36553.27	29047.43	28652.57	28232.88		25949.00			22863.05	22887.54
		3175.856(150)	3216.193(6)		3478.790(100)			3818.862(200)	3952.367(100)	
$z^3F_2^1$	38984.42	31478.50	31083.71		28737 43			26178.41	25294.16	
			3133.920(30)	3177.766(6)		3426.562(200)			3831.840(200)	3828.242(40)
$z^3F_3^1$	39779.99		31879.36	31459.58		29175.43			26089.75	26114.27

z⁴F½	40231.97			3132.767(60) 31911.44			3374.252(50) 29627.72	3425.431(300) 29185.07			3763.13(8) 26566.1
		3206.349(300) 31179.14	3247.478(150) 30784.27	3292.365(10) 30364.59	3515.421(100) 28437.06				3863.056(150) 25878.93	3999.706(8) 24994.80	
z⁴G½	38684.94		3180.290(400) 31434.58	3223.324(100) 31014.94	3436.834(20) 29088.24		3479.567(150) 28731.01	3534.05(10) 28288.1		3898.292(200) 25645.02	3894.56(5) 25669.6
z⁴G½	39335.29			3145.405(500) 31783.23			3388.938(30) 29499.33	3440.589(200) 29056.50			3781.379(200) 26437.90
z⁴G½	40103.60								3069.51(5) 32569.05		
		2939.883(5) 37860.20									
z³P½	45374.95	2560.741(3) 39039.50	2586.911(4) 38644.50							3042.789(15) 32855.05	
z³P½	46545.32										

WASHINGTON, January 29, 1935.